ARCHMAT
Advanced Analytical Methods

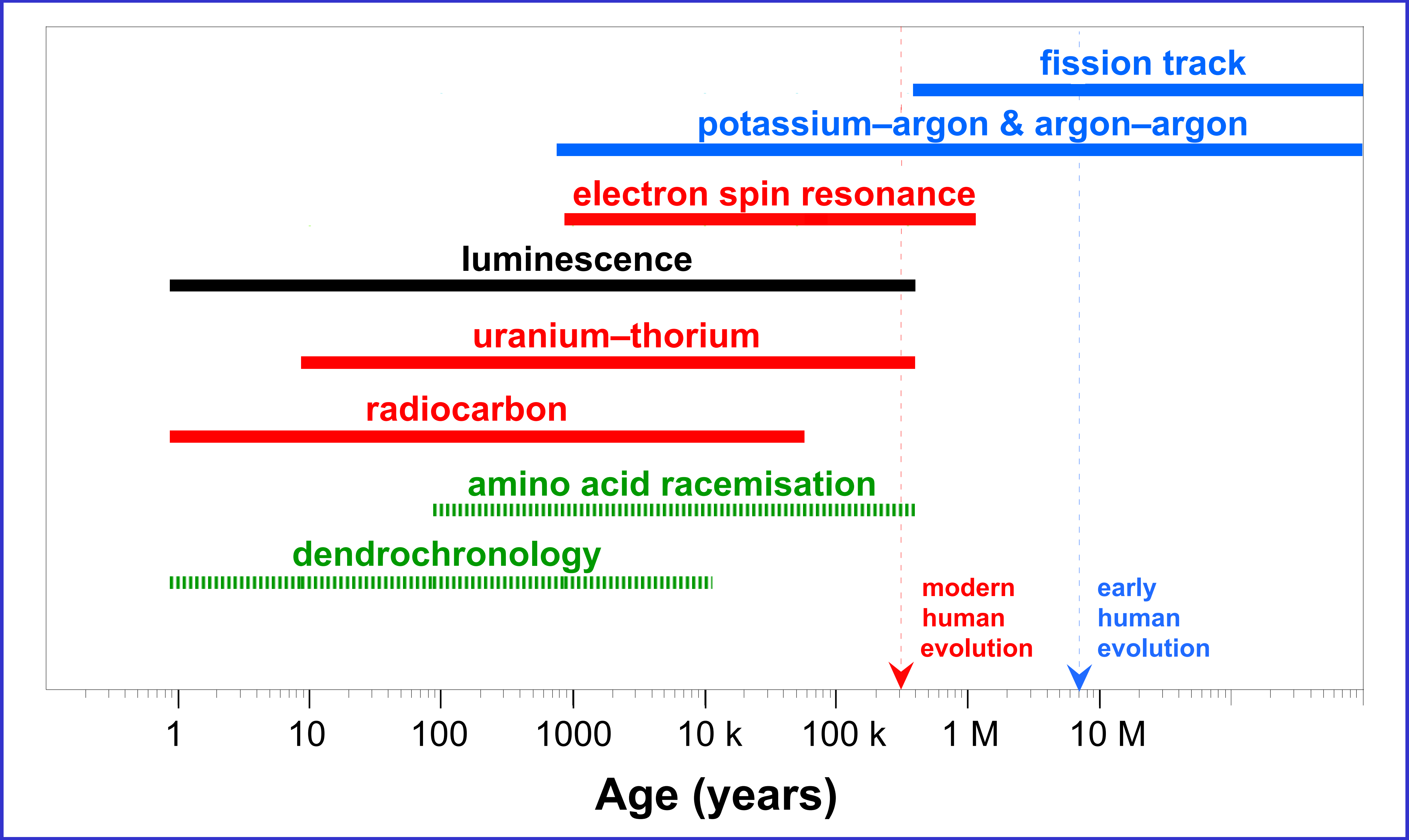
Claudio Tuniz

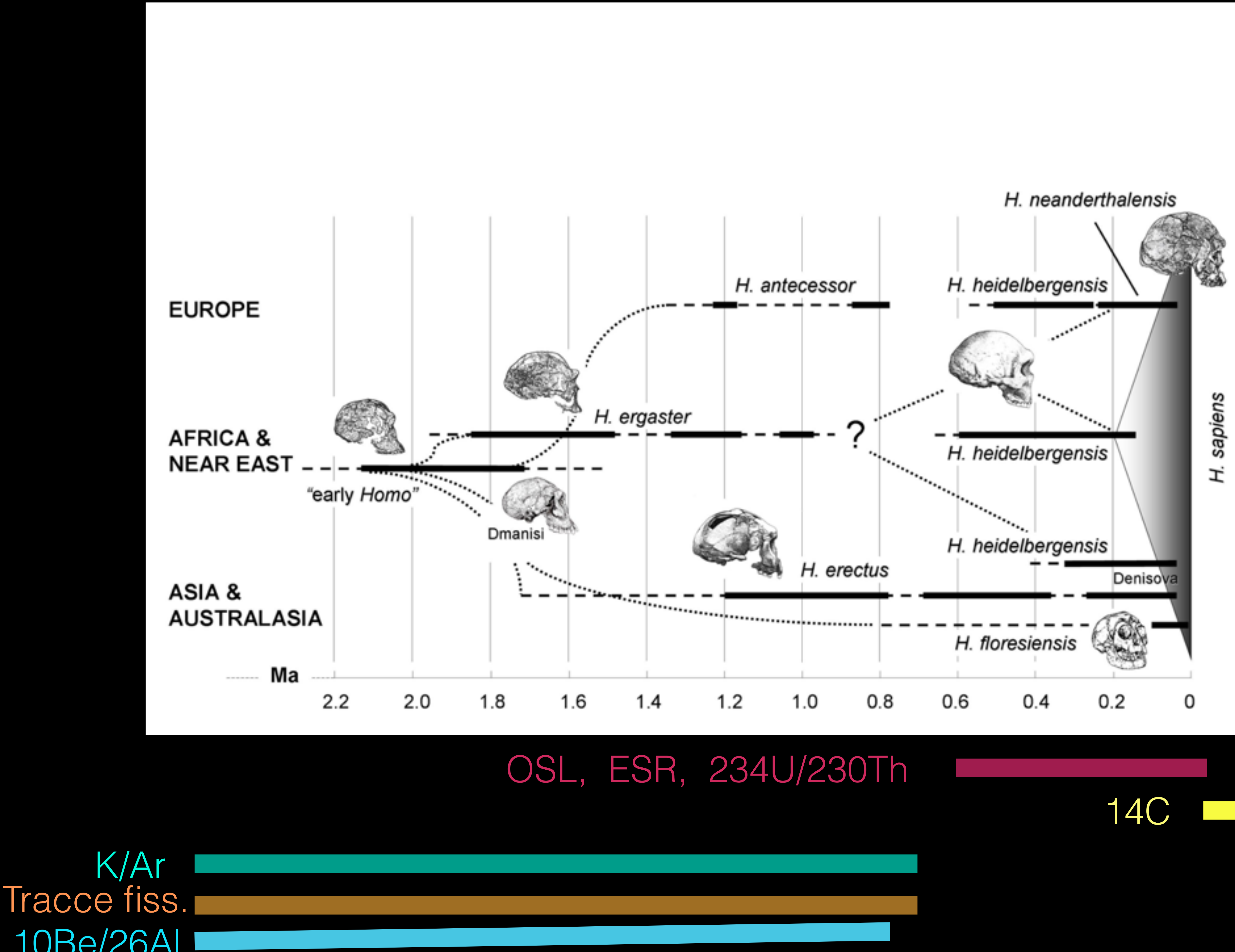
Radiocarbon

Outline

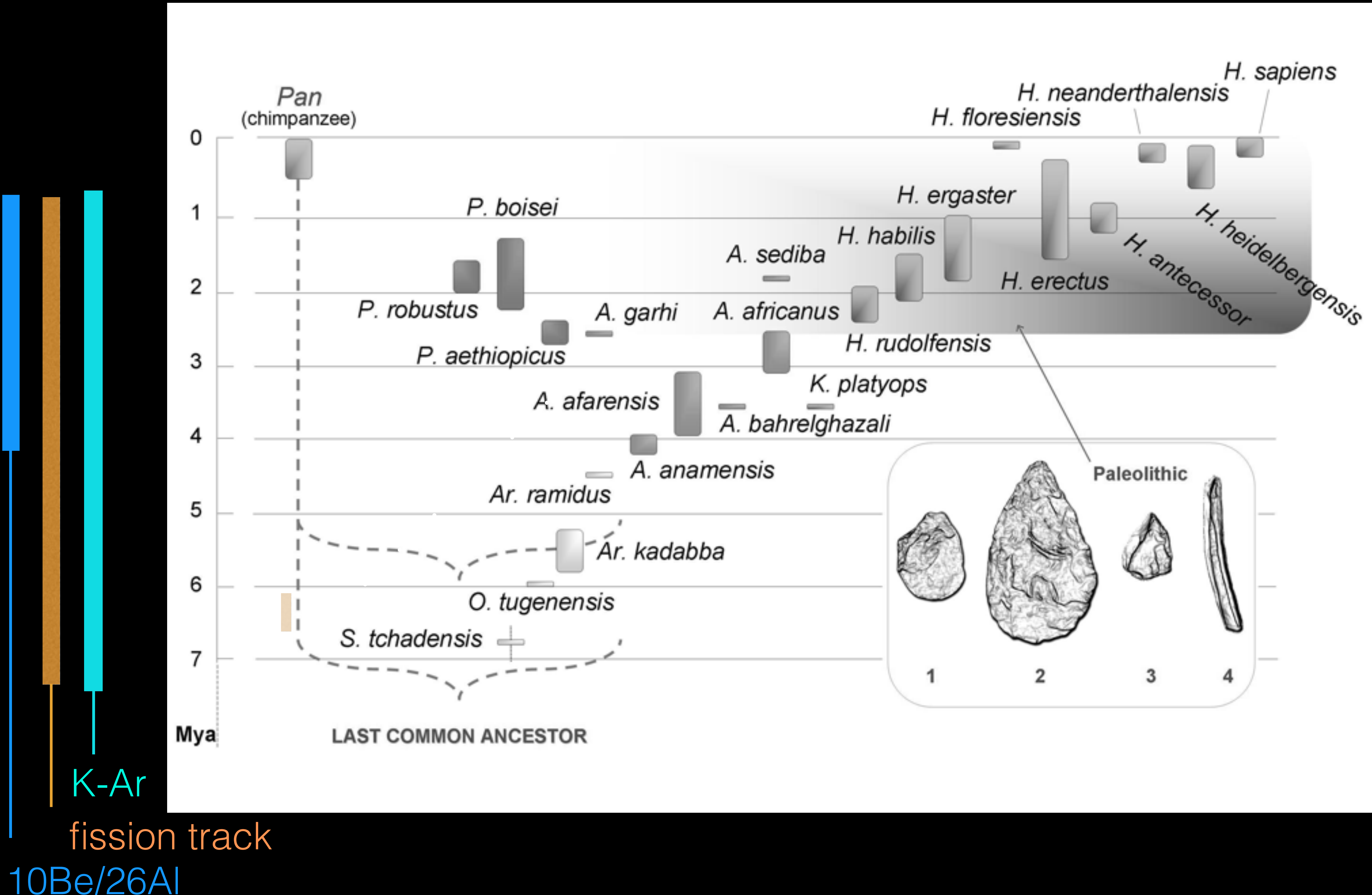
- Introduction
- Principles of radiocarbon dating
- AMS ^{14}C analysis
  - Chemical procedures
  - AMS measurement
  - Calculation of radiocarbon ages
- How to obtain a calendar age

Dating methods





Tuniz Manzi Caramelli - The science of human origins, Laterza, 2013, Left Coast Press, USA, 2014



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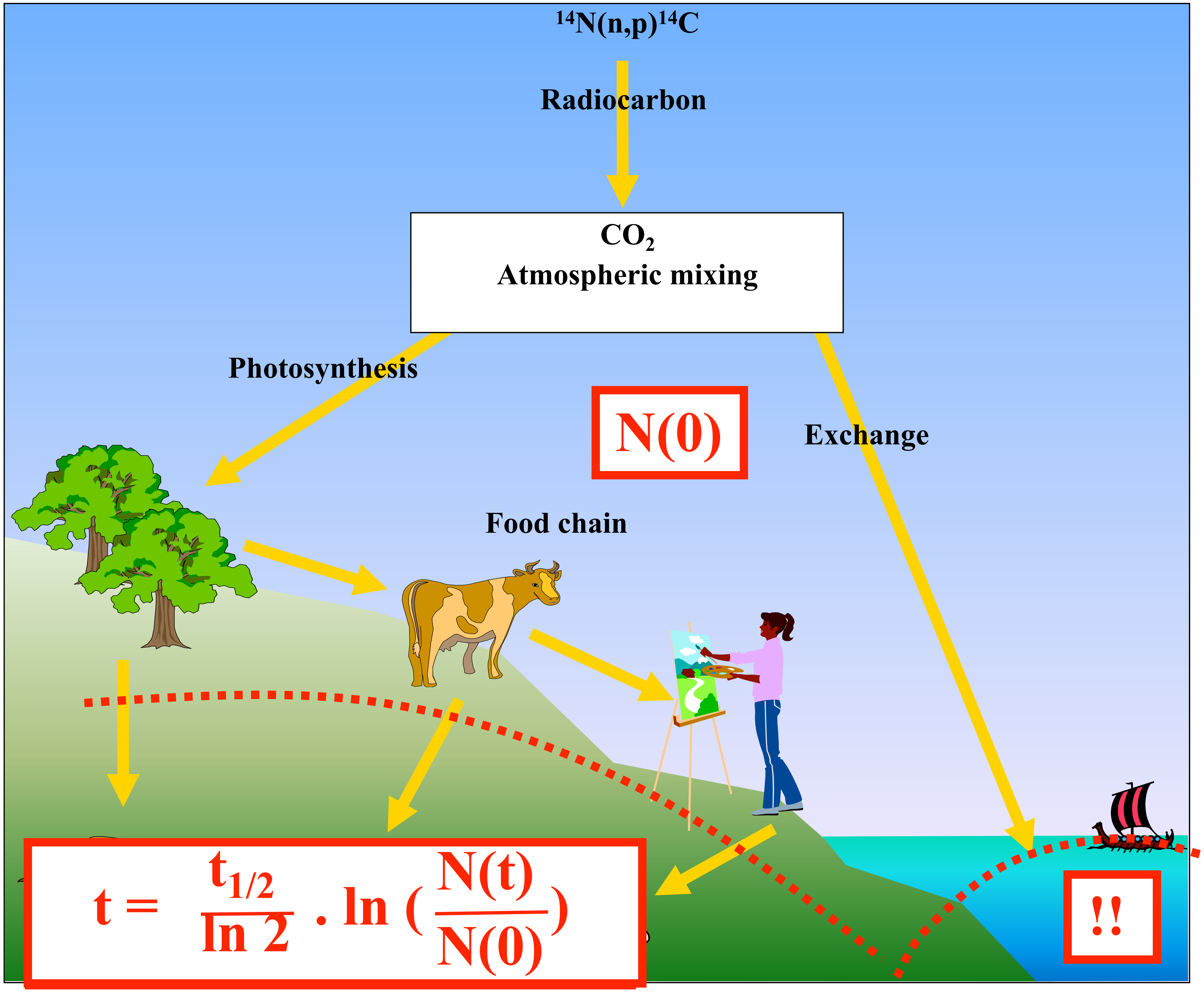
Principles of radiocarbon dating



Radiocarbon dating

Carbon isotopes in nature (modern) :

^{12}C: 98.89% **^{13}C**: 1.11% **^{14}C**: 1.2 x 10^{-10}%

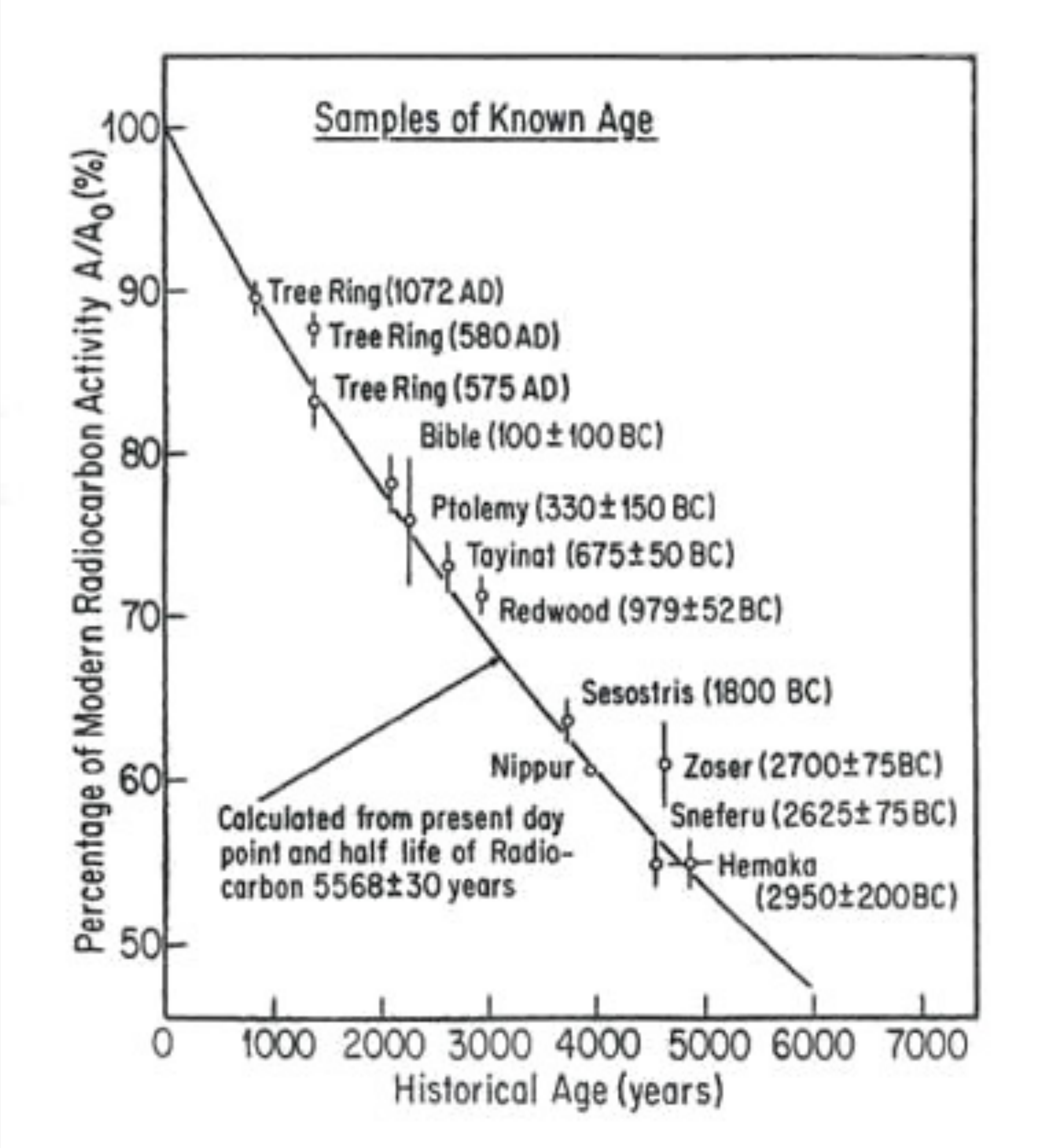
The **radiocarbon method** is based on the rate of decay of ^{14}C, which is formed in the upper atmosphere through the effect of cosmic (thermal) neutrons upon ^{14}N (78% of the atmosphere consists of N_2) via the reaction:

$^{14}N + n \Rightarrow {}^{14}C + p$ **(7.5 kg ^{14}C /yr)**

(σ = 1.8 barn)

"Curve of Knowns" [Arnold and Libby 1949]

The Nobel Prize in Chemistry 1960 to Willard F. Libby "for his method to use carbon-14 for age determination in archaeology, geology, geophysics, and other branches of science".



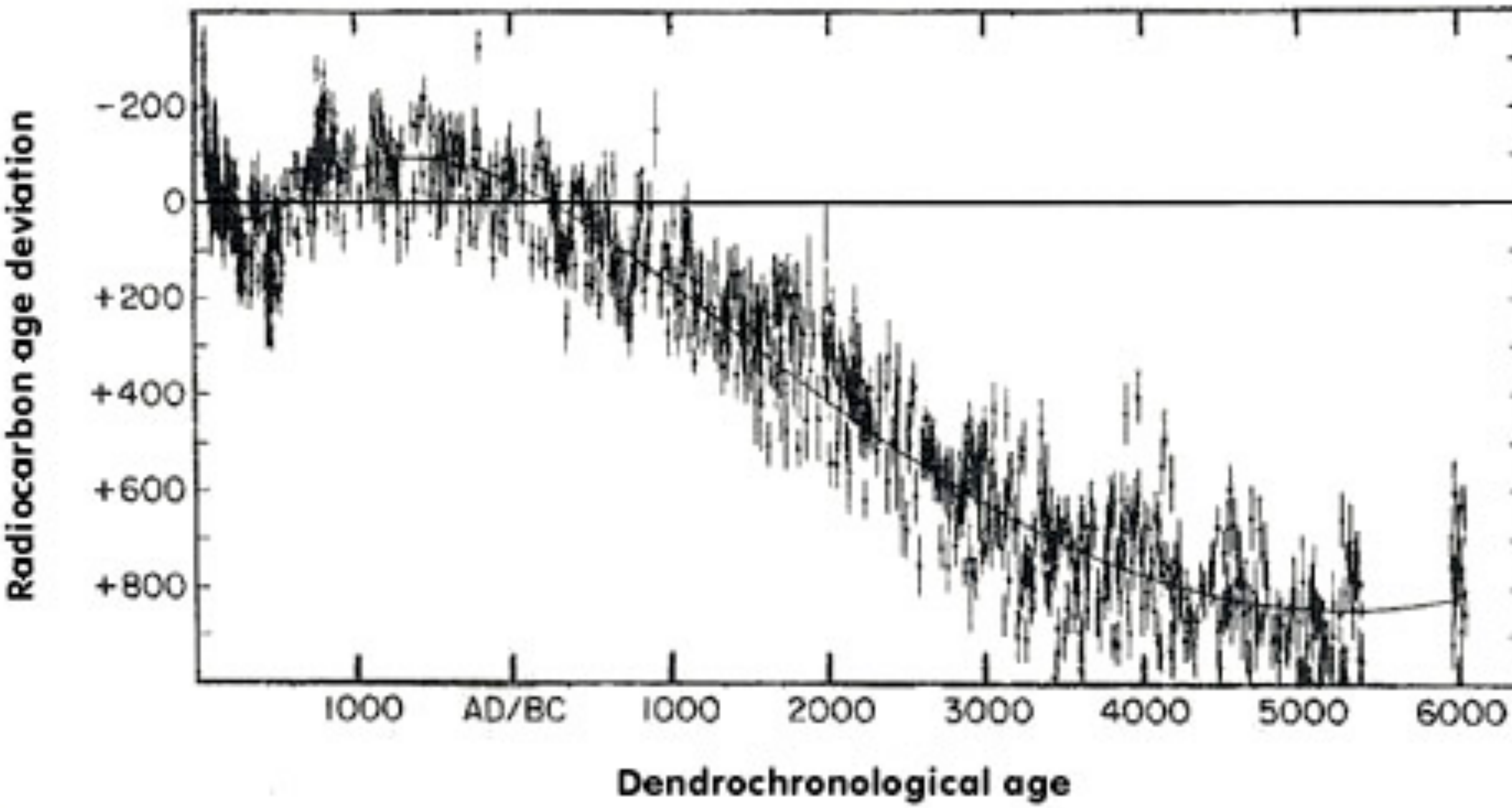
Radiocarbon dating

1950's: further measurements on Egyptian samples of known age point to radiocarbon dates younger than expected … trust historical data or radiocarbon dates?

1960: ^{14}C in tree rings show ^{14}C fluctuations up ± 5% over last 1500 years

1958: de Vries s 'wiggles' identified. Also long term fluctuations.

Difference between expected and measured 14C content in tree-rings



1960-1980
"Second Radiocarbon Revolution:" Calibration

- Calibration of ^{14}C time scale: Distinguishing "real (solar, sidereal) time" and "^{14}C time"

- Bristlecone pine / ^{14}C data: First detailed continuous tree ring-based data set documenting ^{14}C offsets over last 7000 yrs. »

- Long-term anomaly: maximum Holocene offset about 10% or ~800 years at about 7000 BP

- Shorter-term anomalies: "De Vries effects" multi-millennial and multi-century oscillations in ^{14}C time spectrum

1977

Conventional Radiocarbon Age: Definition

- Stuiver and Polach (1977) Reporting of ^{14}C Data. *Radiocarbon*

1. Use Libby half-life (5568 years)

2. Use 0.95 NBS Oxalic Acid I [or standards with known relationship] to define "zero" age ^{14}C count rate

3. Use A.D. 1950 as 0 BP

4. Normalize ^{14}C activity to common $\delta^{13}C$ value = -25.0 ‰

5. Uncalibrated - defines "radiocarbon time" expressed in "^{14}C years"

Principles of radiocarbon dating

Stable Isotopes

			99%	1%			
$^{9}_{6}C$	$^{10}_{6}C$	$^{11}_{6}C$	$^{12}_{6}C$	$^{13}_{6}C$	$^{14}_{6}C$	$^{15}_{6}C$	$^{16}_{6}C$
.13 sec.	19 sec.	20.6 min.			5730 years	2.25 sec.	.74 sec.

Positron decay (${}^{9}C$, ${}^{10}C$, ${}^{11}C$) — βeta decay (${}^{14}C$, ${}^{15}C$, ${}^{16}C$)

^{14}C production $n + {}^{14}N \longrightarrow {}^{14}C + p$

^{14}C decay ${}^{14}C \longrightarrow {}^{14}C + \beta$ +antineutrino

$T_{1/2}$ = 5730 years

- Equilibrium ${}^{14}C/{}^{12}C \sim 1.2 \times 10^{-12}$

Measurement techniques

Solid carbon method (Libby)

↓

Gas counting

↓

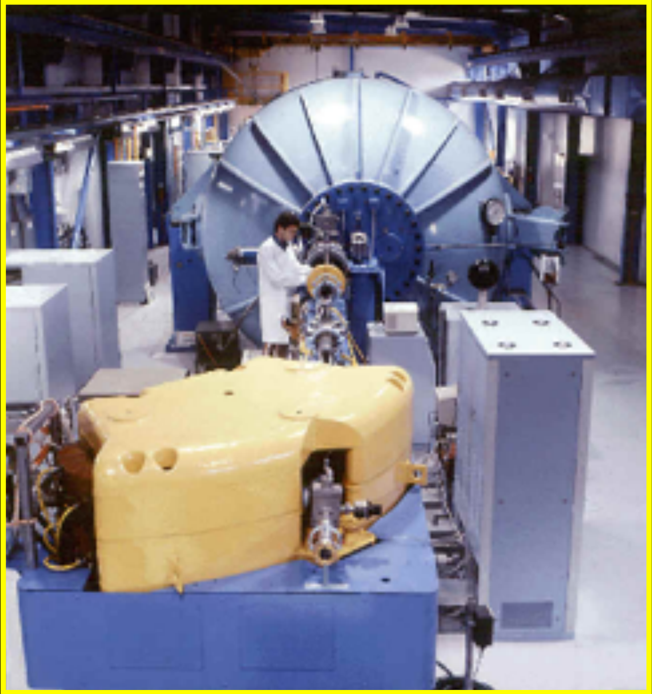
Liquid scintillation counting

↓

AMS: counting atoms rather than decays

Principles of radiocarbon dating

Detect radiation



Count atoms

Modern sample, 1% precision

Detect radiation	Count atoms
10^4 decays	10^4 counts
1g C	1 minute
1000 minutes	100 μg used

Principles of radiocarbon dating

AMS advantages over decay counting

Large machines (size is getting smaller)

High efficiency

Shorter counting time

Small mass (contamination)

Principles of radiocarbon dating

Sample Type	Examples	Decay counting	AMS
Charcoal		2 – 5 g	50 – 200 mg
Wood		5 – 10 g	50 – 100 mg
Marine shell (carbonates)		10 – 20 g	30 - 60 mg
Plant products	Paper, textitles, seeds, grains	5 – 10 g	50 – 100 mg
Animal products	Bone, tusk, ivory, teeth	100 – 500 g	500 – 2000 mg
	Skin, hair	50 – 300 g	50 – 100 mg
Sediment	Peat, soil organics	10 g	10 – 500 mg

Datable materials and their sample size requirements for ^{14}C analysis

Chemical procedures

Pre-treatment

Chemical procedures

Pre-treatment

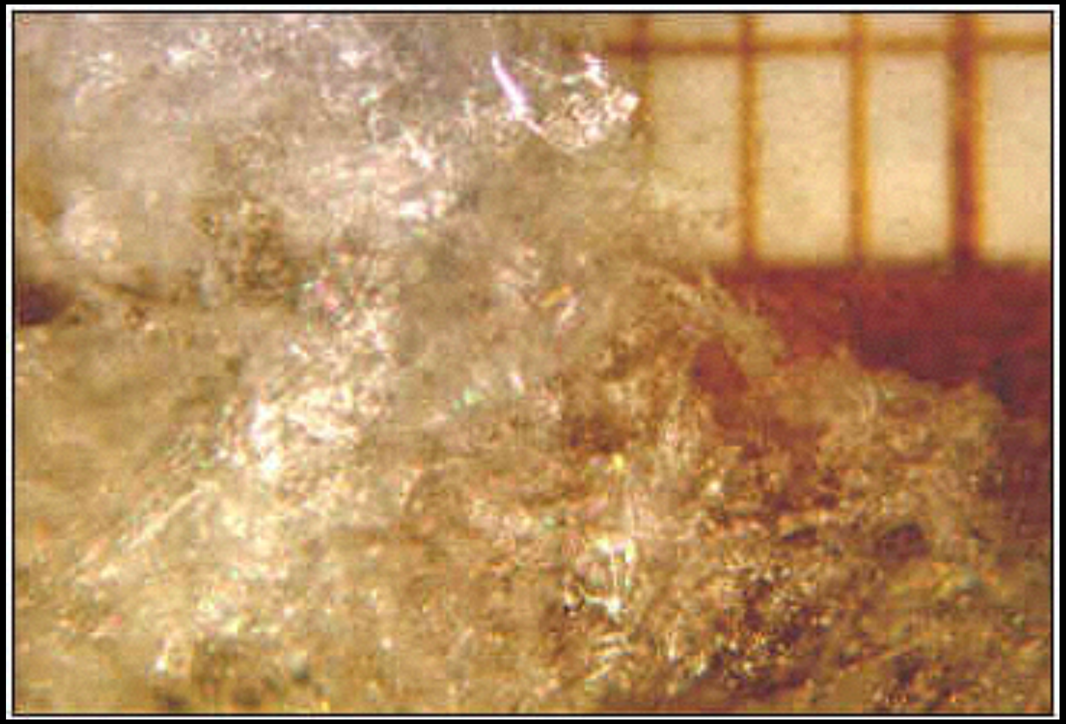
Extraneous carbon is removed

Chemical procedures

Pre-treatment

Extraneous carbon is removed

Specific component is isolated



Chemical procedures

Pre-treatment

Extraneous carbon is removed

Specific component is isolated

Carbon isolation

Chemical procedures

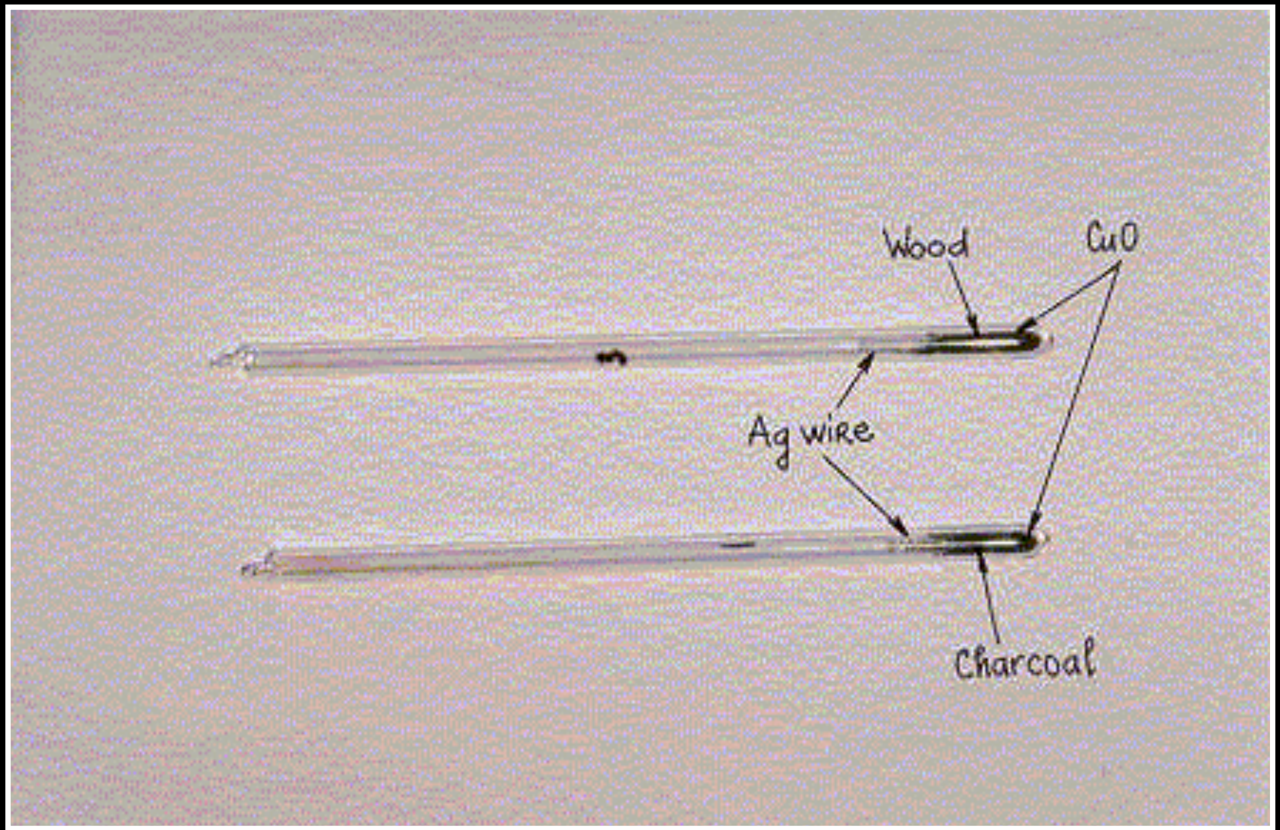
Pre-treatment

Extraneous carbon is removed

Specific component is isolated

Carbon isolation

Combustion (organic samples)



Chemical procedures

Pre-treatment

Extraneous carbon is removed

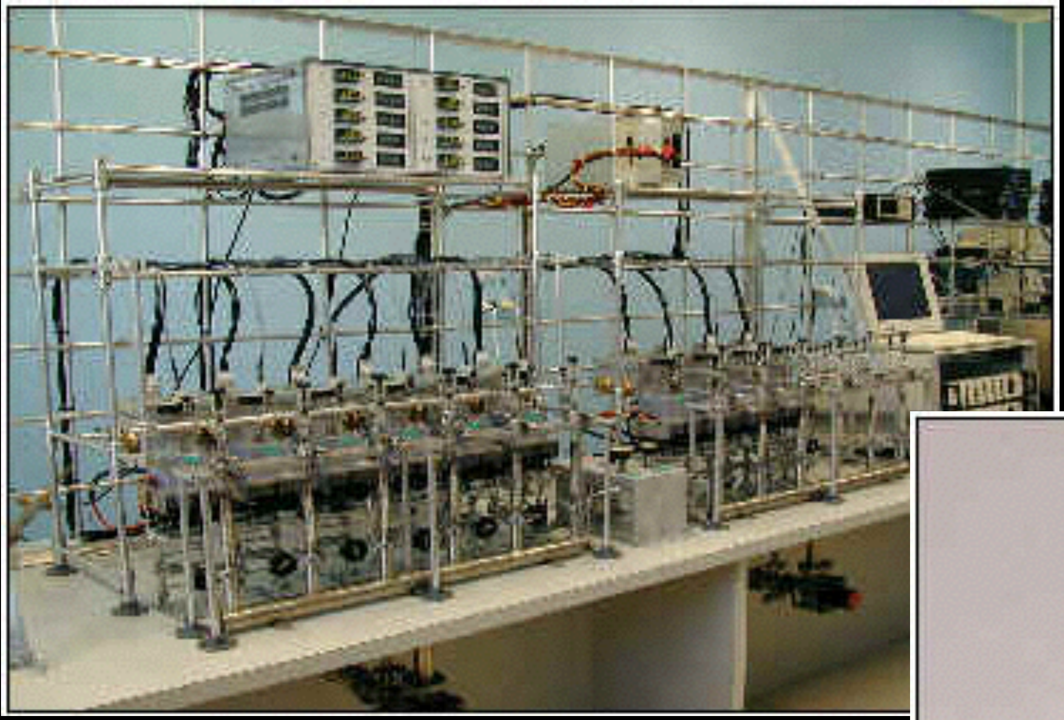
Specific component is isolated

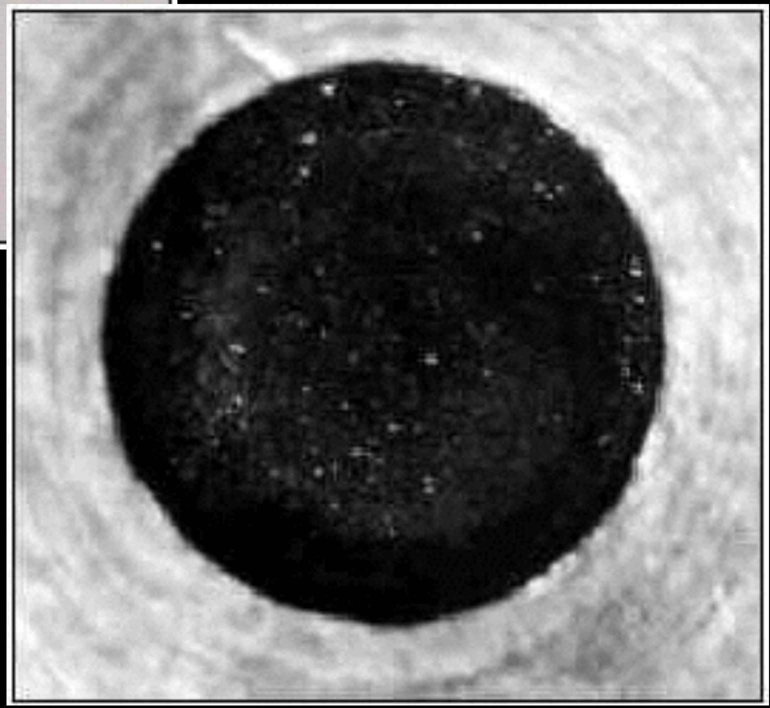
Combustion (organic samples)

Hydrolysis (inorganic samples)

Graphitisation

Chemical procedures

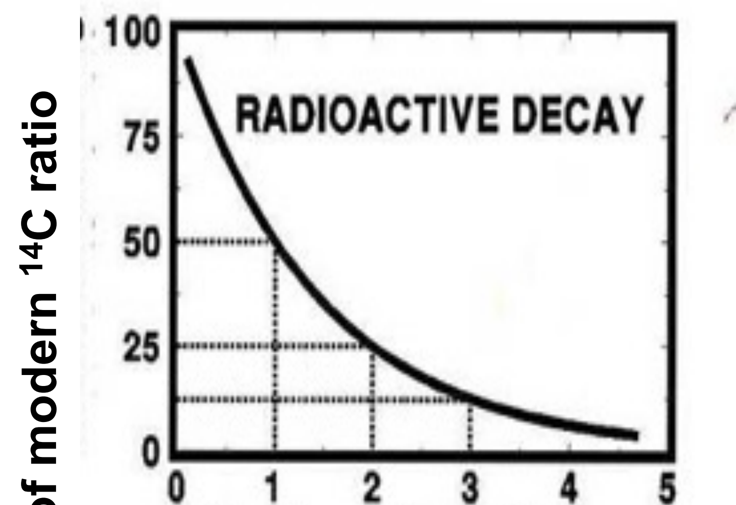




Graphitisation

high-energy primary galactic proton

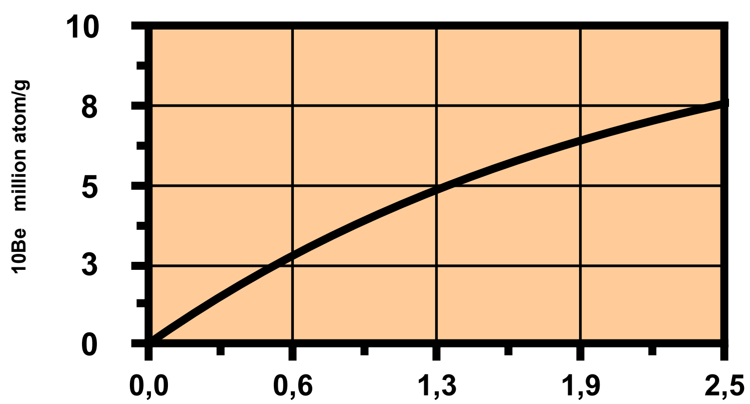
(1) Atmospheric production



$$C = C_O\, e^{-\lambda T}$$

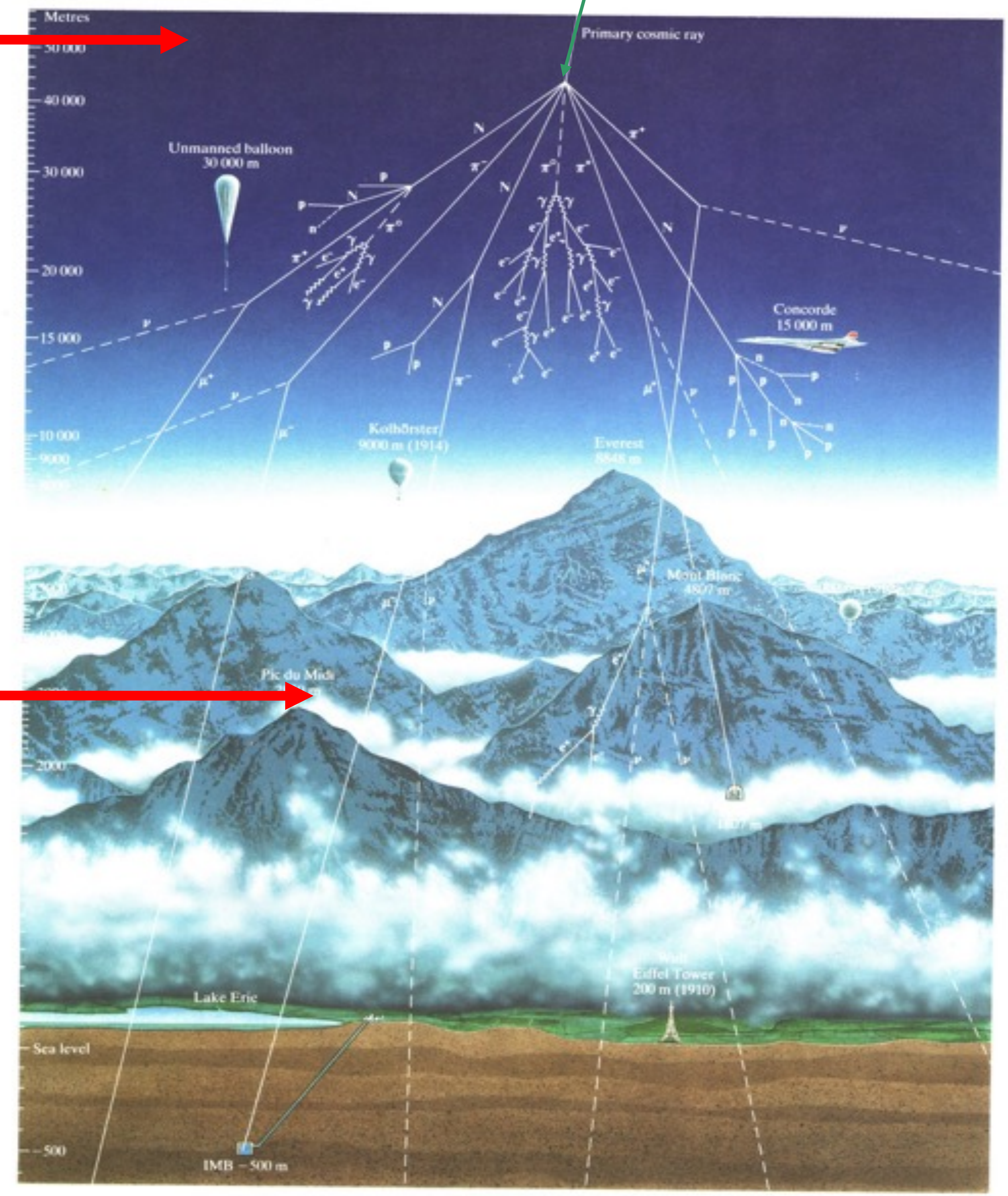
T = Radiocarbon dating

(2) Surface production



$$C = P / \lambda\, (1 - e^{-\lambda T})$$

T = Exposure dating



^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl

$T_{1/2}$ ~ 5 ka - 1.5 Ma

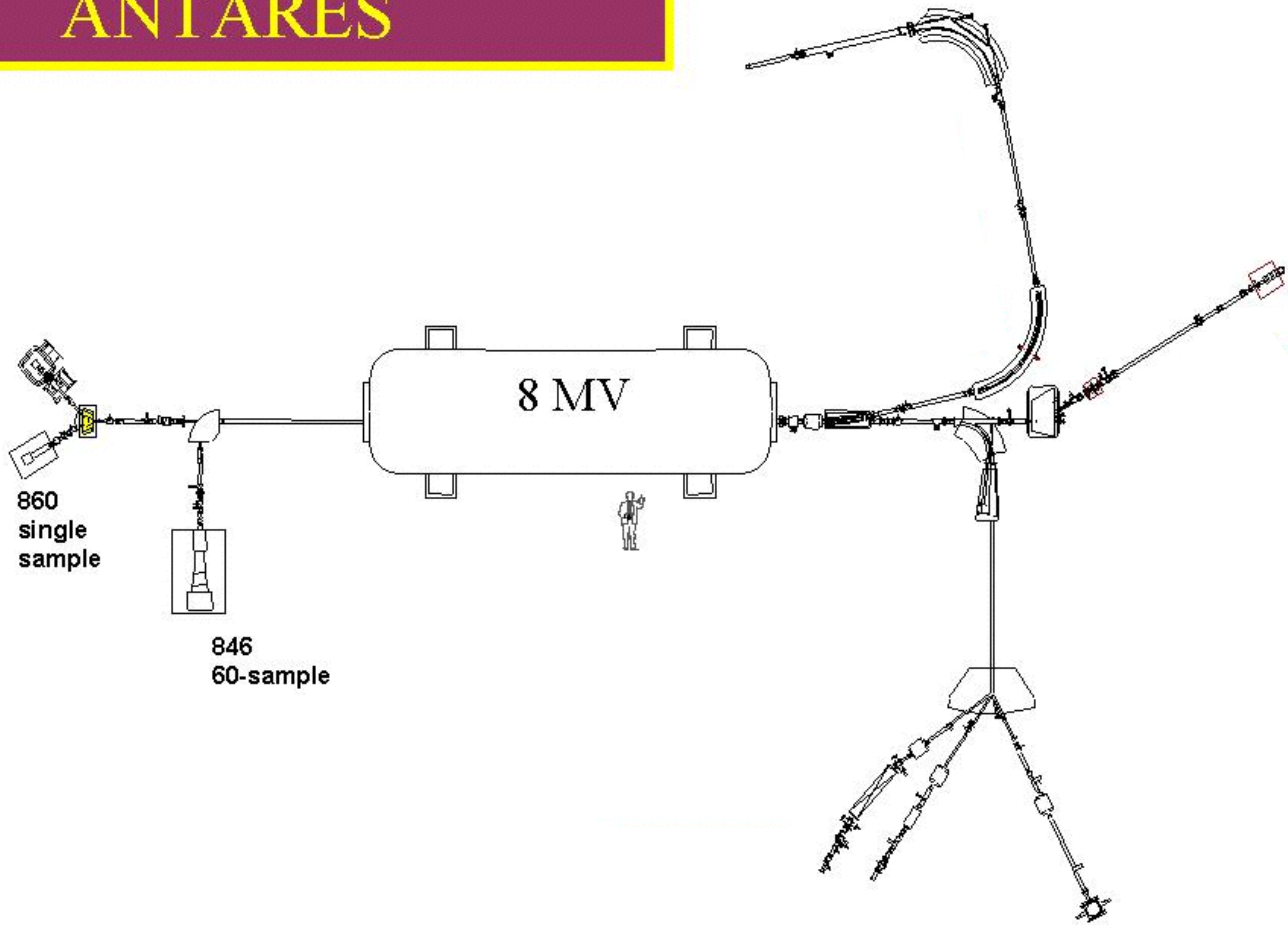
Accelerator Mass Spectrometry

What is AMS

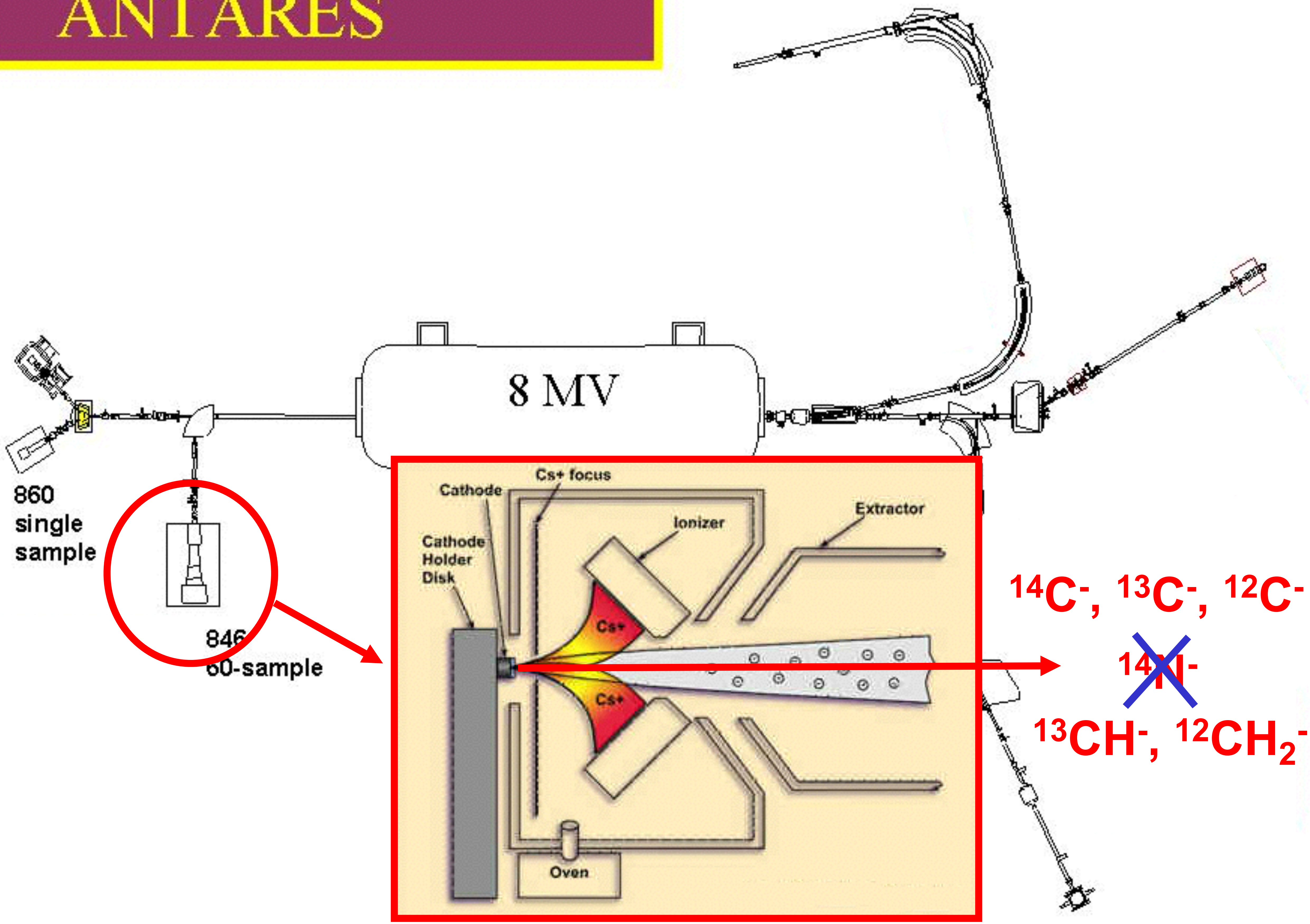
- **ultra-sensitive analytical technique to identify and count rare atoms of long-lived radionuclides produced by cosmic rays in the atmosphere and at Earth's surface using a ion-beam accelerator at an unprecedented sensitivity of 1:10^{-15} after elimination of all molecular, isotopic and isobaric interferences**

1. extract atoms from sample
2. place sample in a negative ion-source
3. accelerate ions to high energies (millions of volts)
4. reject backgrounds with magnetic and electrostatic deflectors
5. identify and count radioisotope via mass, energy & nuclear charge

ANTARES

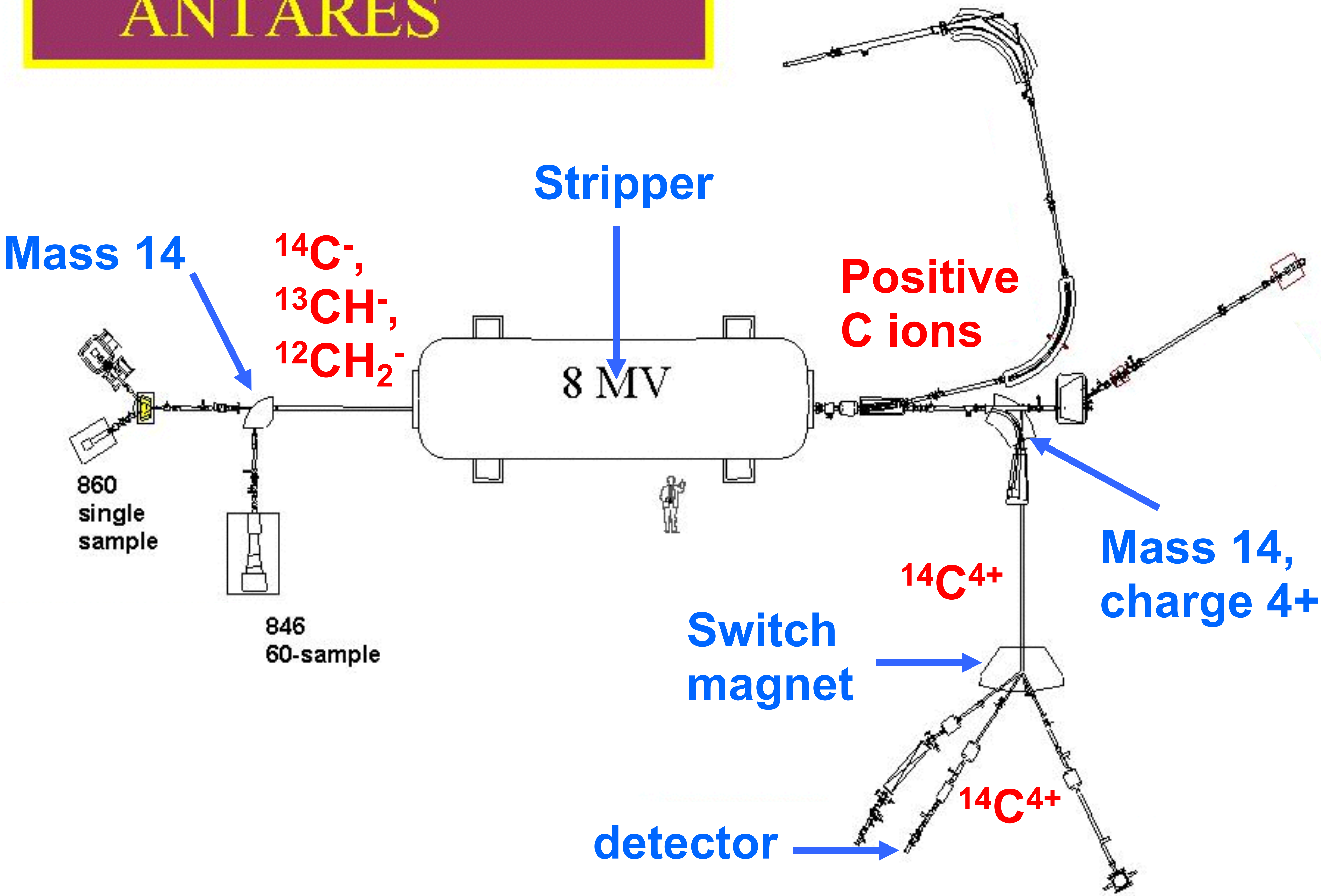


ANTARES



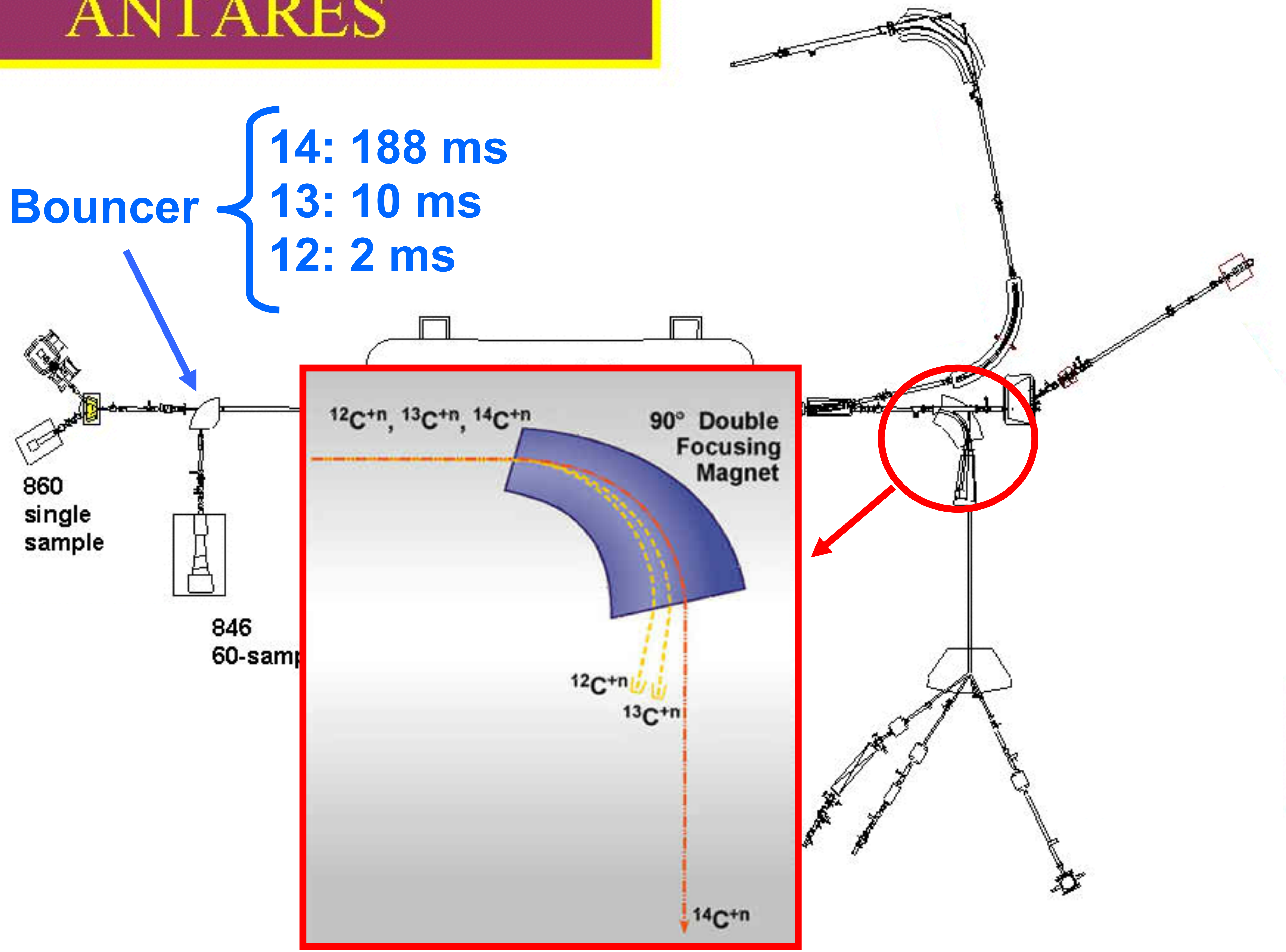
8 MV
860
single
sample
846
60-sample
Cs+ focus
Cathode
Ionizer
Extractor
Cathode
Holder
Disk
Cs+
Cs+
Oven
$^{14}C^-$, $^{13}C^-$, $^{12}C^-$
$^{14}N^-$
$^{13}CH^-$, $^{12}CH_2^-$

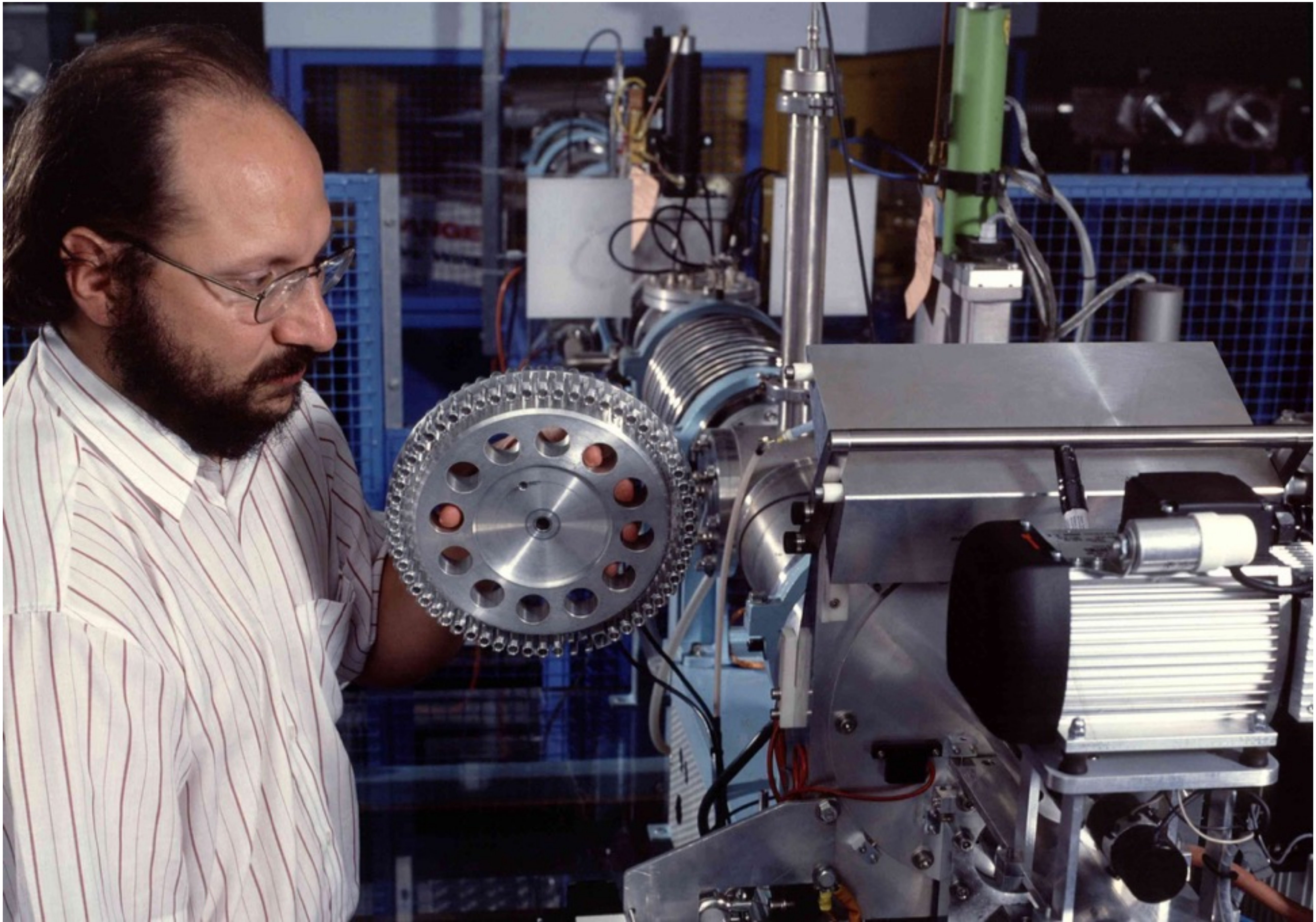
ANTARES



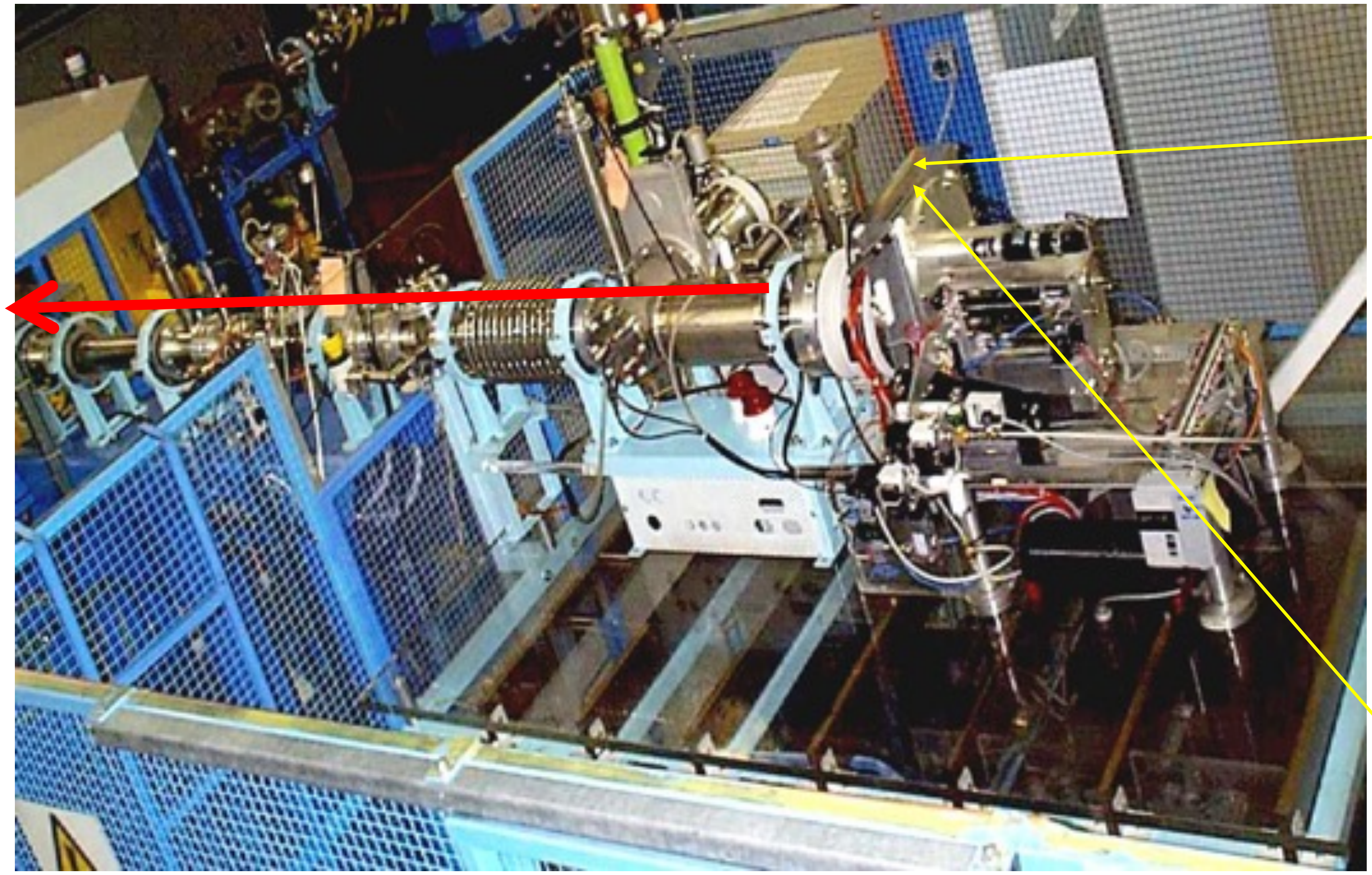
Mass 14
$^{14}C^-$,
$^{13}CH^-$,
$^{12}CH_2^-$
Stripper
8 MV
Positive
C ions
860
single
sample
846
60-sample
Mass 14,
charge 4+
$^{14}C^{4+}$
Switch
magnet
$^{14}C^{4+}$
detector

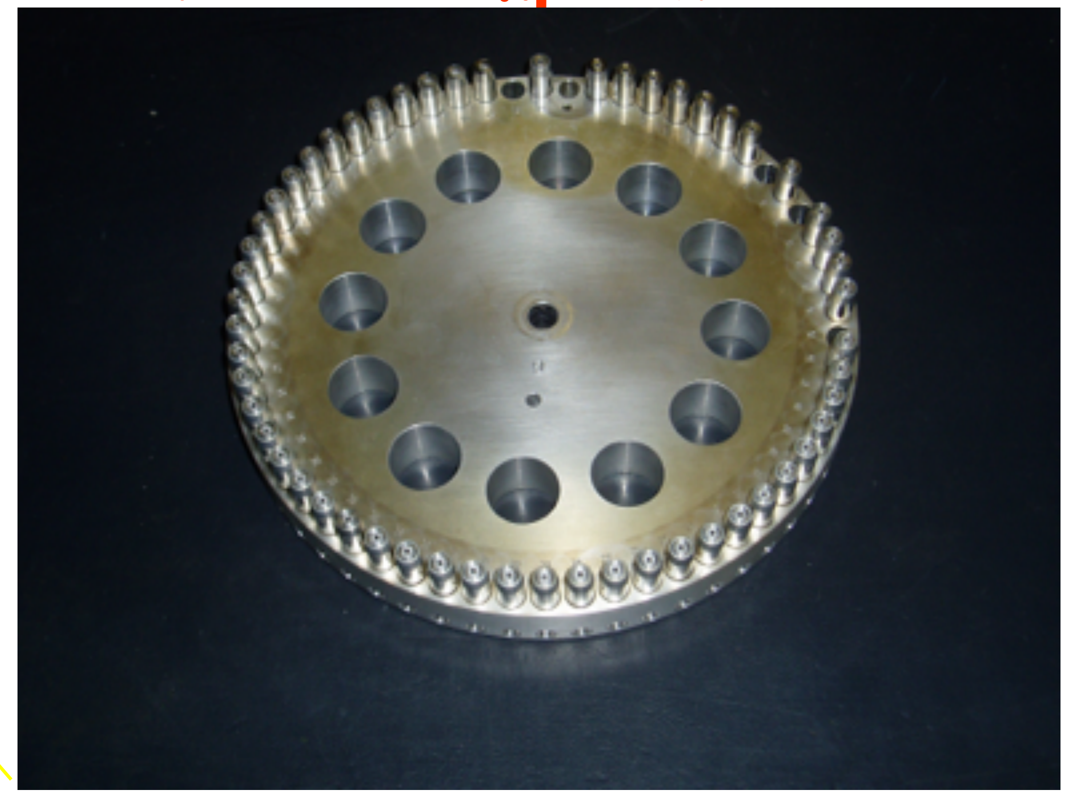
ANTARES


Bouncer
14: 188 ms
13: 10 ms
12: 2 ms
860
single
sample
846
60-samp
$^{12}C^{+n}$, $^{13}C^{+n}$, $^{14}C^{+n}$
90° Double
Focusing
Magnet
$^{12}C^{+n}$
$^{13}C^{+n}$
$^{14}C^{+n}$



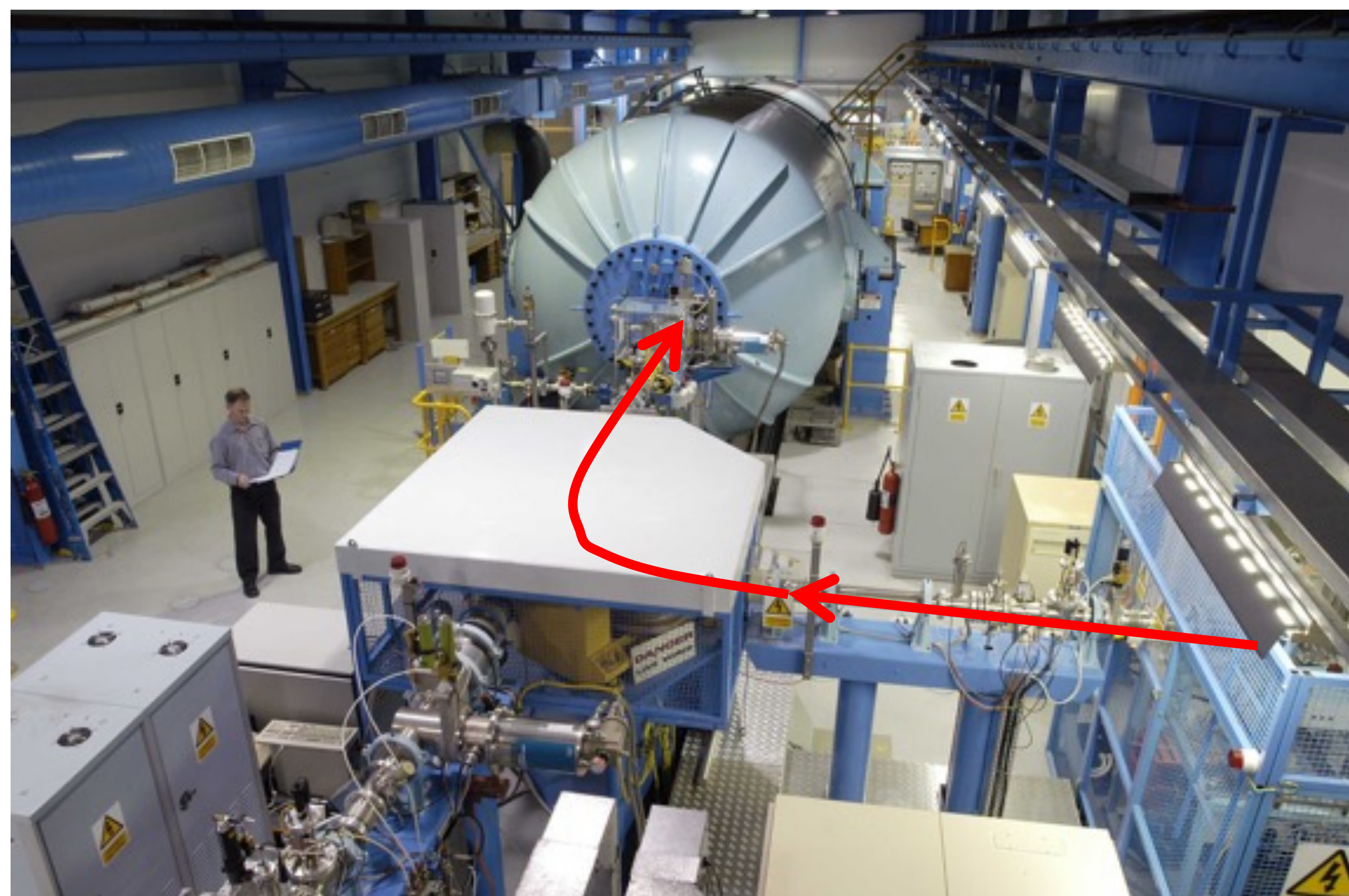
AMS 60 sample wheel

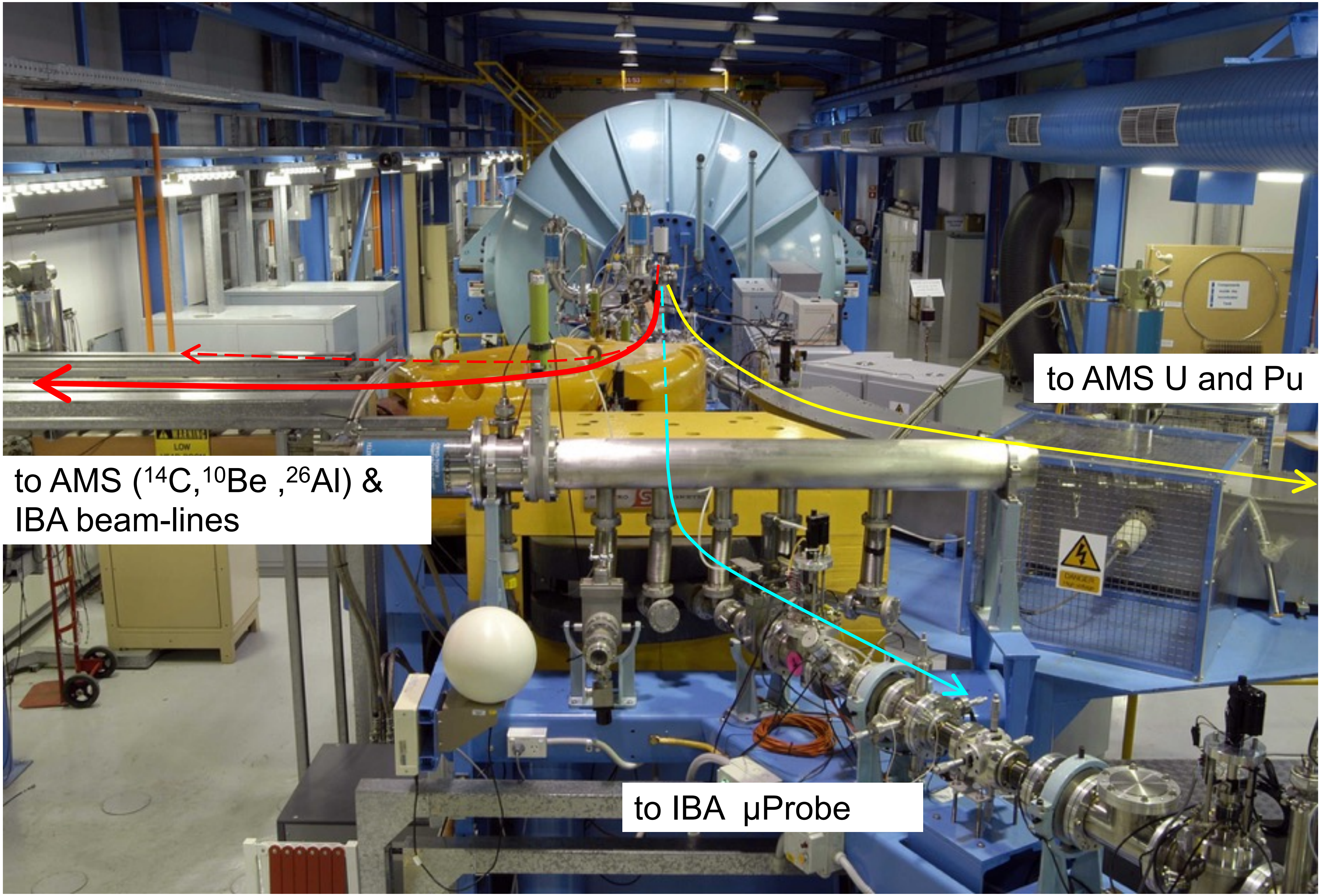




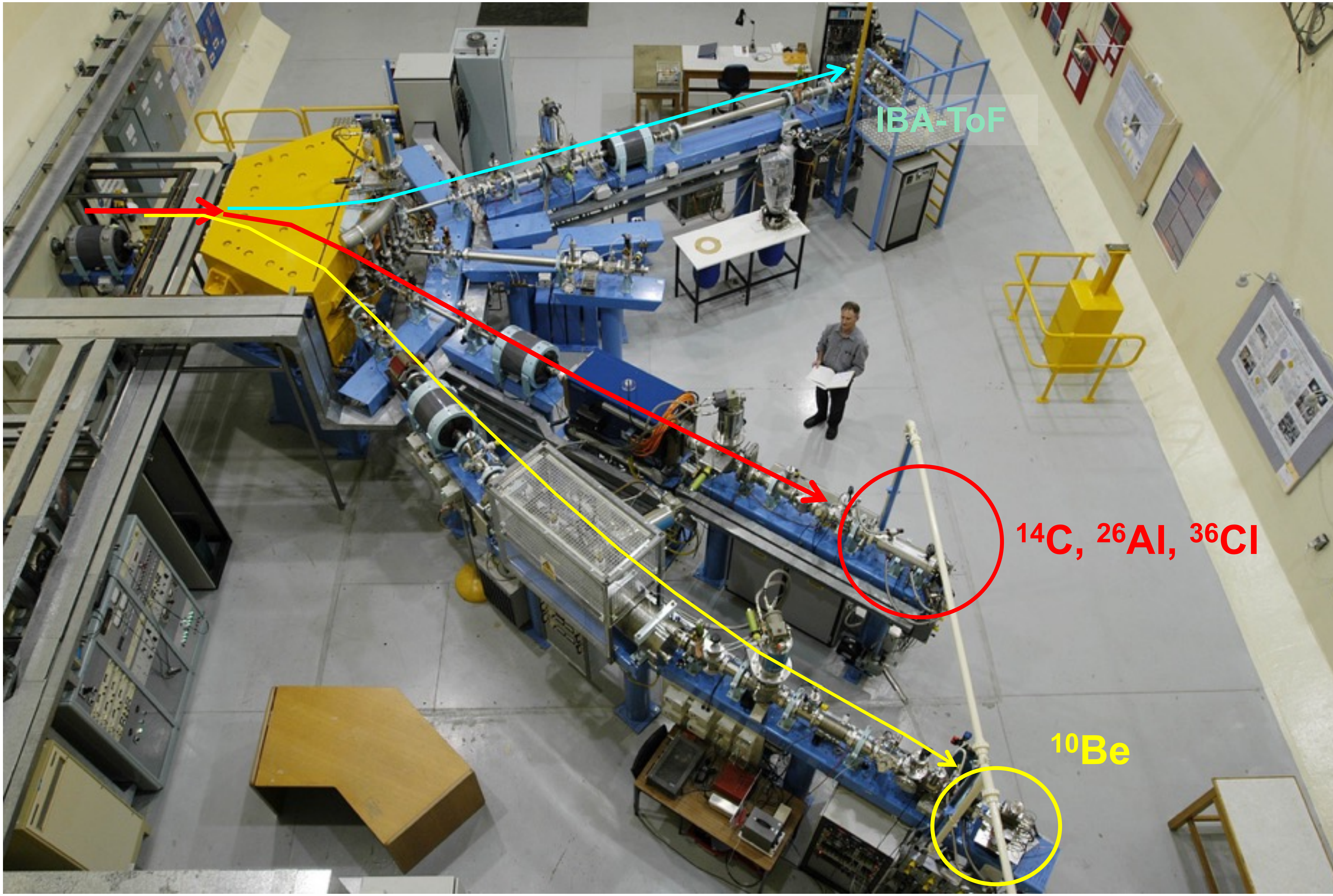
Ion-source injector

Low-energy

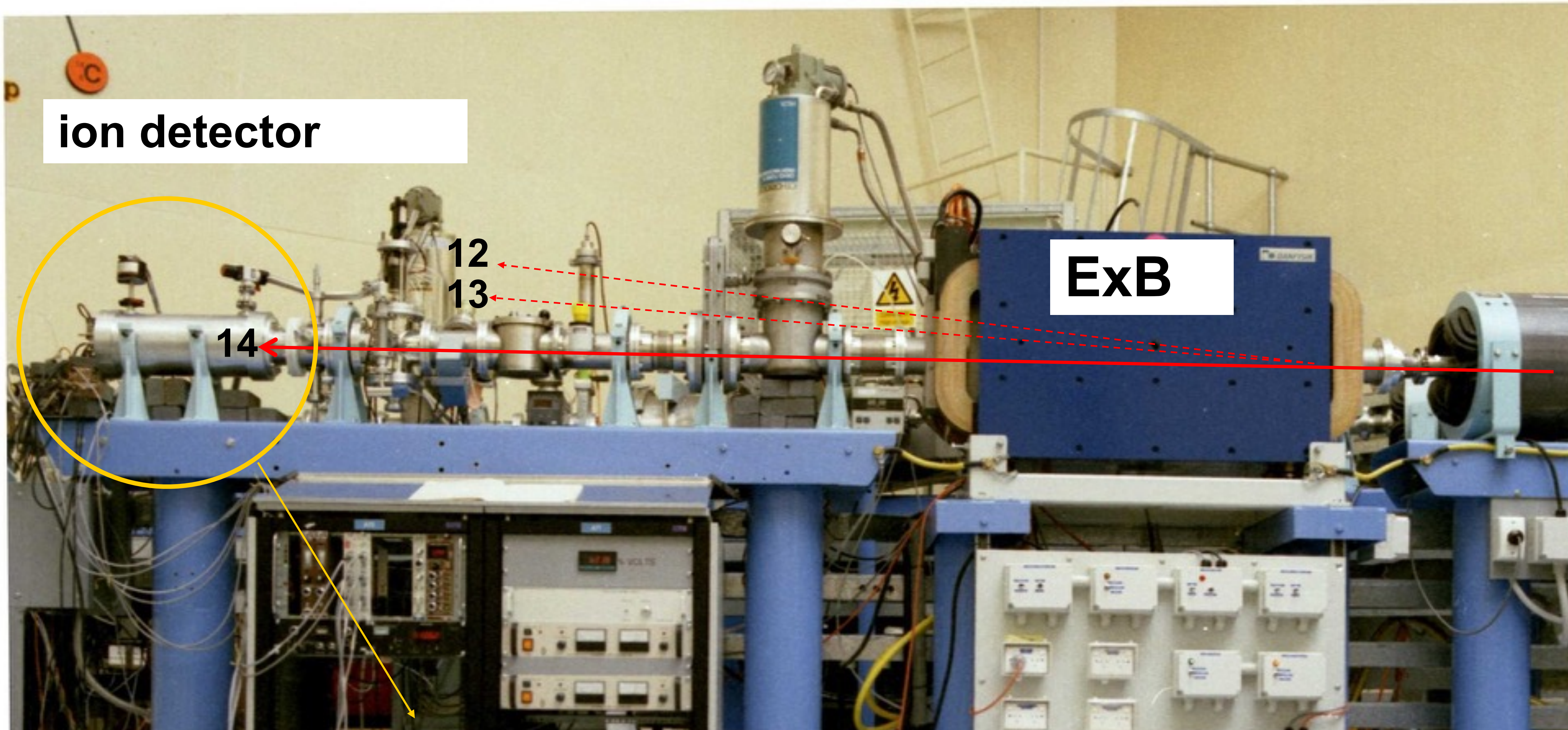



to AMS U and Pu
to AMS (^{14}C, ^{10}Be , ^{26}Al) &
IBA beam-lines
to IBA µProbe

High-energy



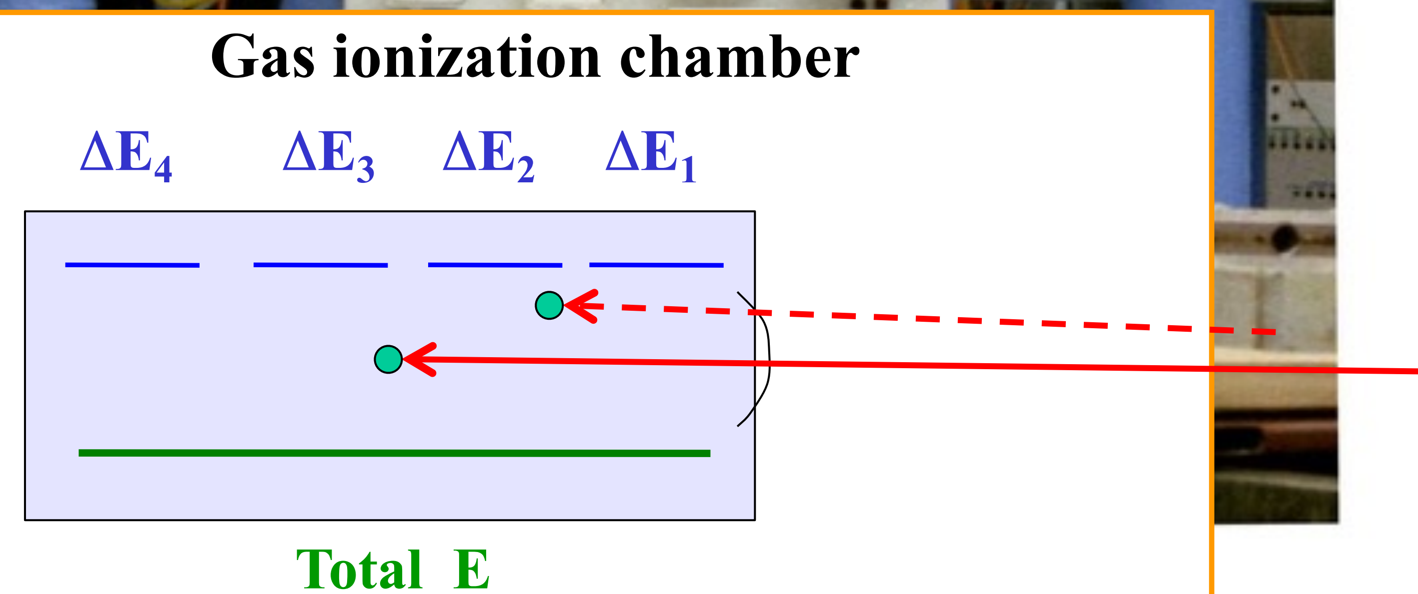
Beam-lines

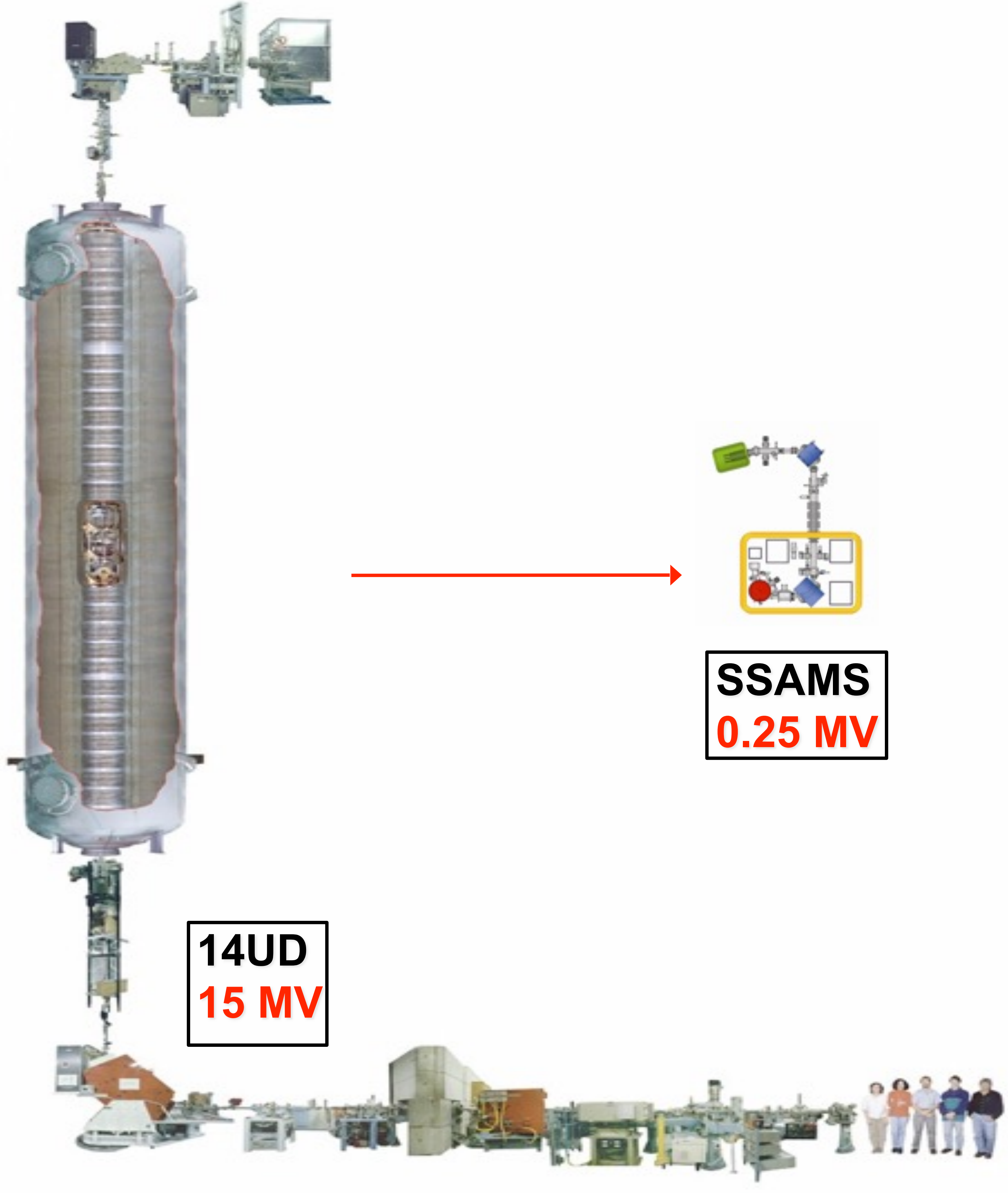


Energy loss rate in gas detector

dE/dX = f (Z, M)

Z protons, Mass of nucleus




SSAMS
0.25 MV
14UD
15 MV

Counting atoms… rather than decays

1 hair (>90% keratin)

Keratin --- (42%) -->1 mg C = 5×10^{19} ^{12}C atoms

5×10^{7} ^{14}C atoms

^{14}C -- β --> ^{14}N 1 β decay/hour

AMS 6×10^{5} ^{14}C atoms/hour

(*) human hair acquired from 4 grave lots had to be combined in the first dating of human hair (from the egyptian pre-dynastic site of Nagoda)

[Lybby, 1955]

Radiocarbon age

Conventional Radiocarbon Age

- Radiocarbon ages are reported in years before present (**BP**) which, by international agreement, is before AD 1950.
- Laboratories use an agreed standard for the **modern reference level** of ^{14}C, and a **half-life of 5,568 years** for ^{14}C.
- Radiocarbon ages are corrected for **isotopic fractionation**, using either an estimated value or a mass-spectrometric measurement of the $^{13}C/^{12}C$ ratio of a subsample.
- **Conventional radiocarbon ages** are NOT corrected for past variations in the ^{14}C content of the atmosphere, nor for any regional or reservoir effects. This must be done separately.

Radiocarbon calculations

Conventional Age = $-\tau \ln F = -8033 \ln (A_{SN} / A_{ON})$

A_{SN} measured activity of the sample corrected for fractionation
A_{0N} standard modern activity corrected for fractionation and

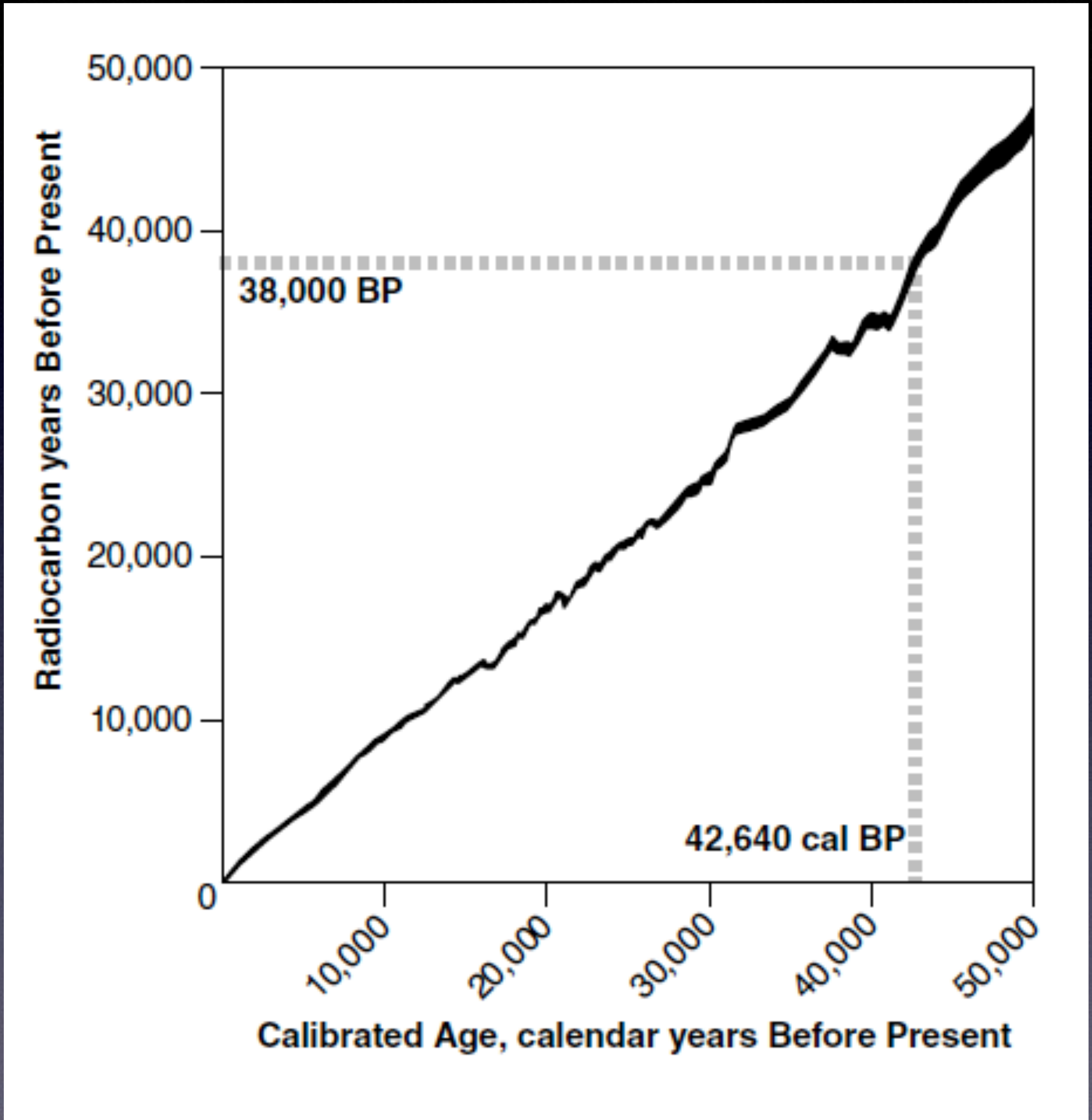
F (A_{SN} / A_{ON}) is the measured "fraction of modern" for a sample S

The fact that the conventional age is calculated with an incorrect half-life is rectified when conventional ages are converted to calibrated ages

Radiocarbon calibration

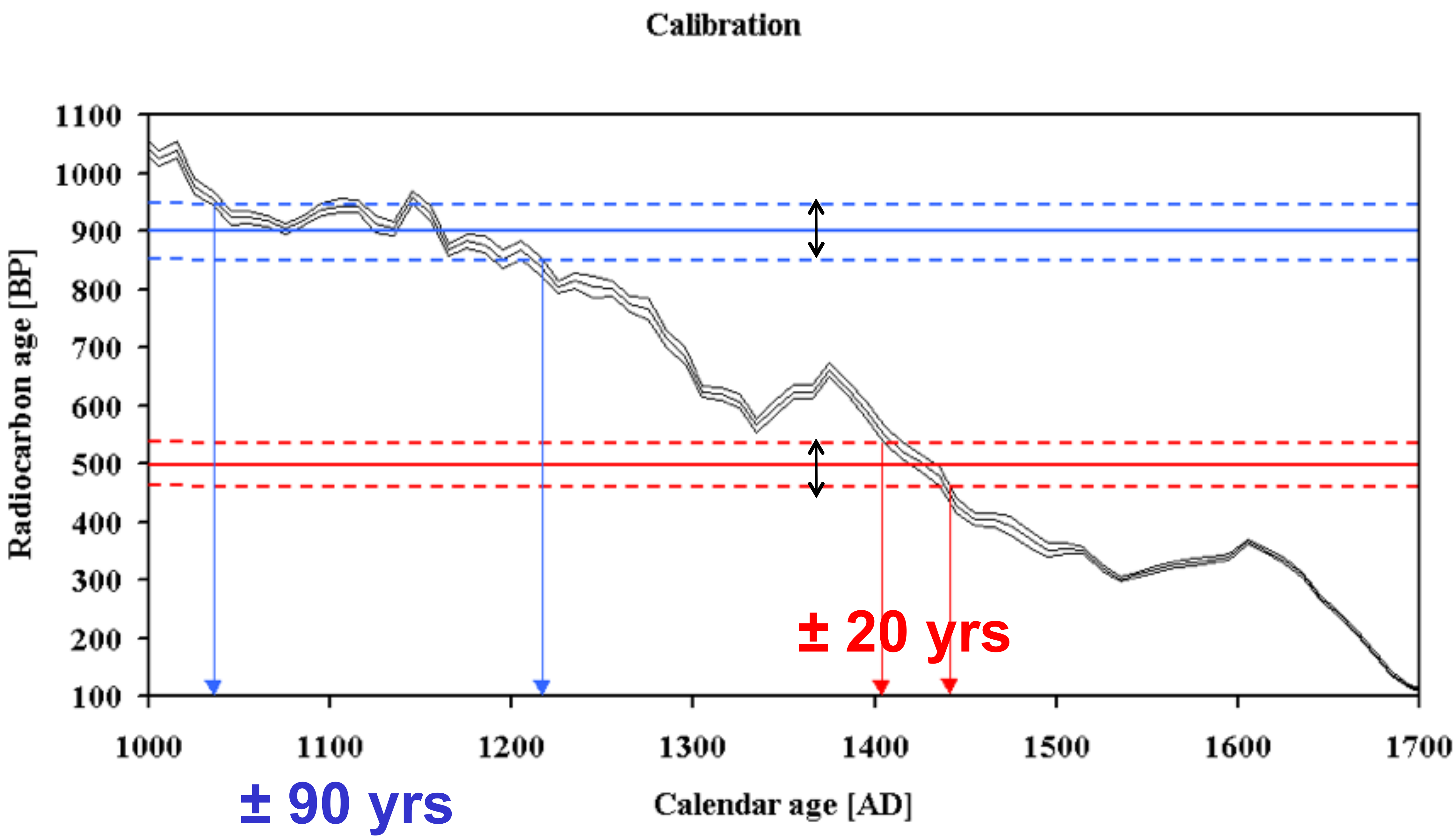
- The calibration curve is based on dendrochronologically-dated tree rings for the period 0-12,400 cal yr before present (BP, with 0 BP being AD 1950).
- For the remaining period 12,400-26,000 cal yr BP, the curve is derived from independently dated marine samples such as foraminifera and corals.
- A new internationally-ratified calibration curve (IntCal09) covering the whole radiocarbon timescale (~50,000 cal yr) has been produced by the IntCal Working Group.

Radiocarbon calibration

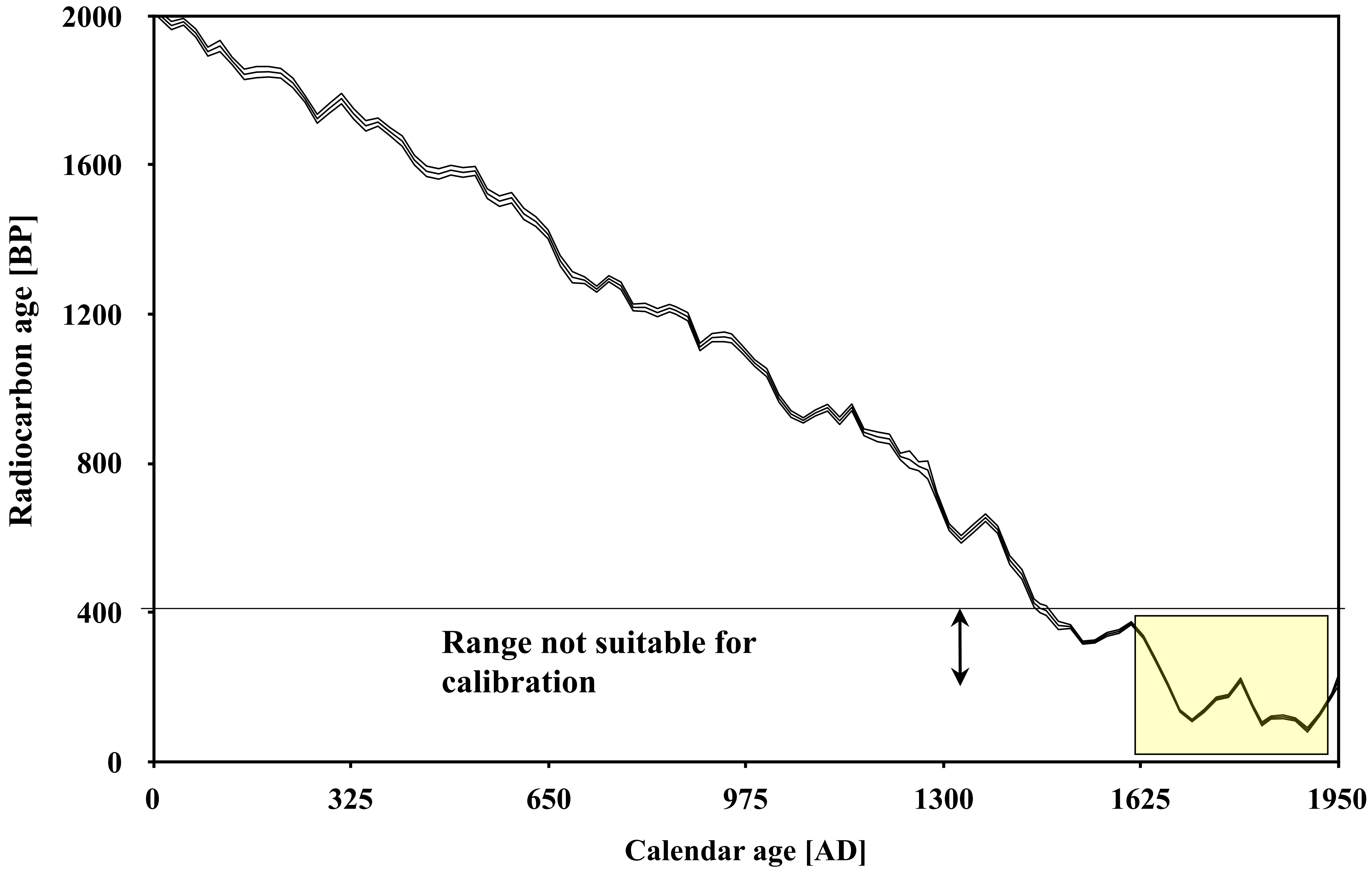


Tuniz Manzi Caramelli - The Science of Human Origins 2014

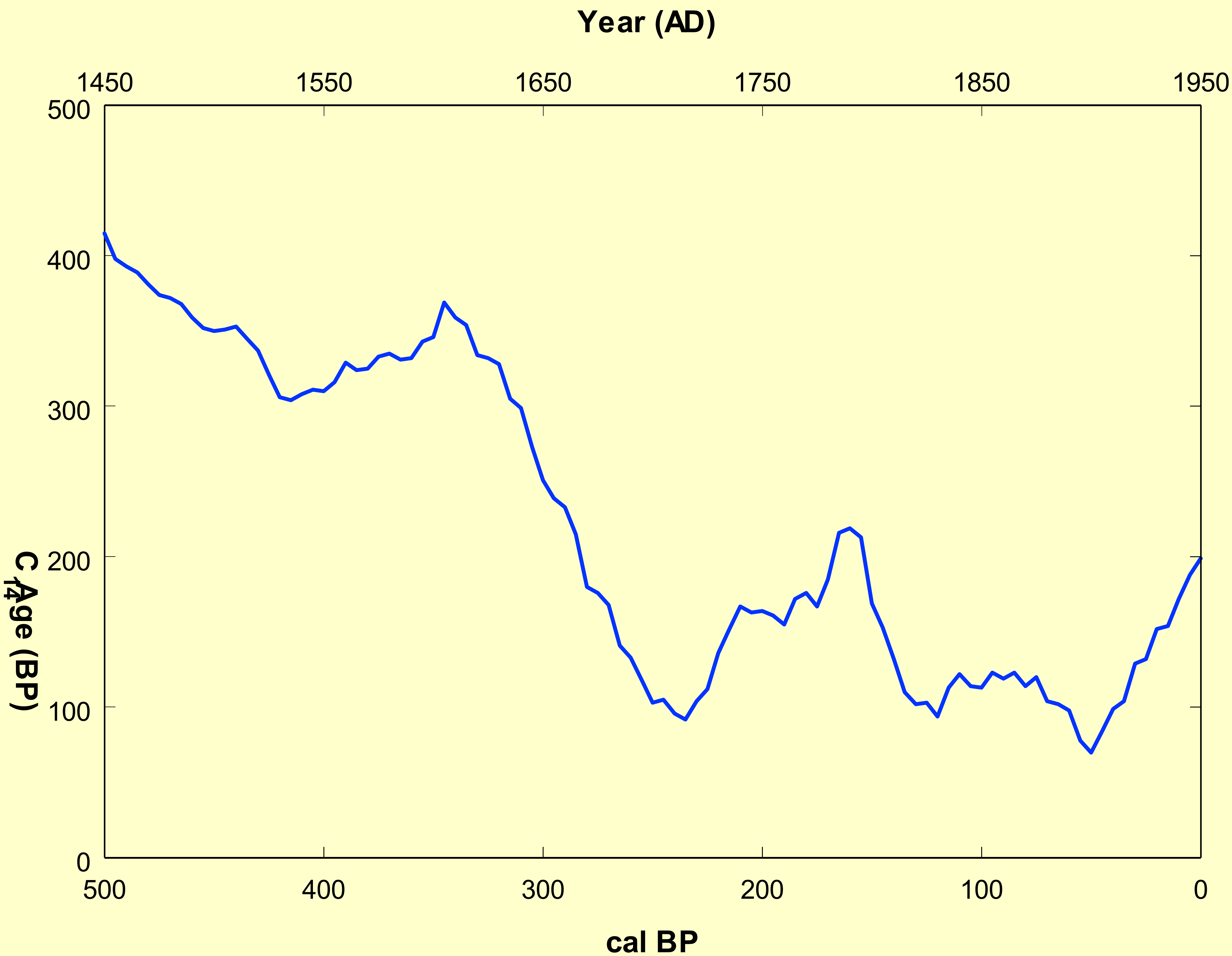
AMS $^{14}C/^{12}C$ results ± 0.5%
this means radiocarbon age error is ± 40-50 years



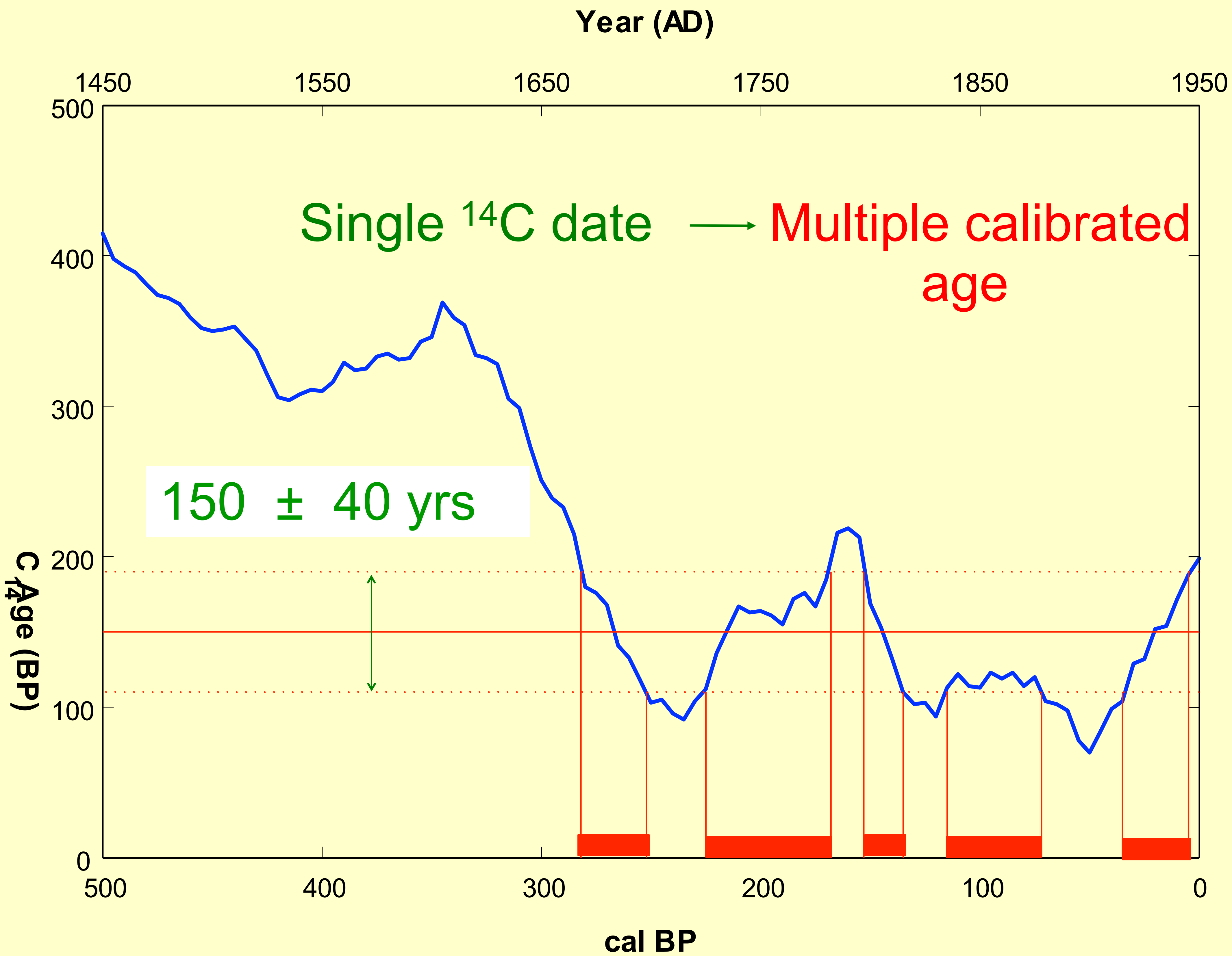
The last 2,000 years for 14C calibration



IntCal04 Calibration curve - Last 500 yrs

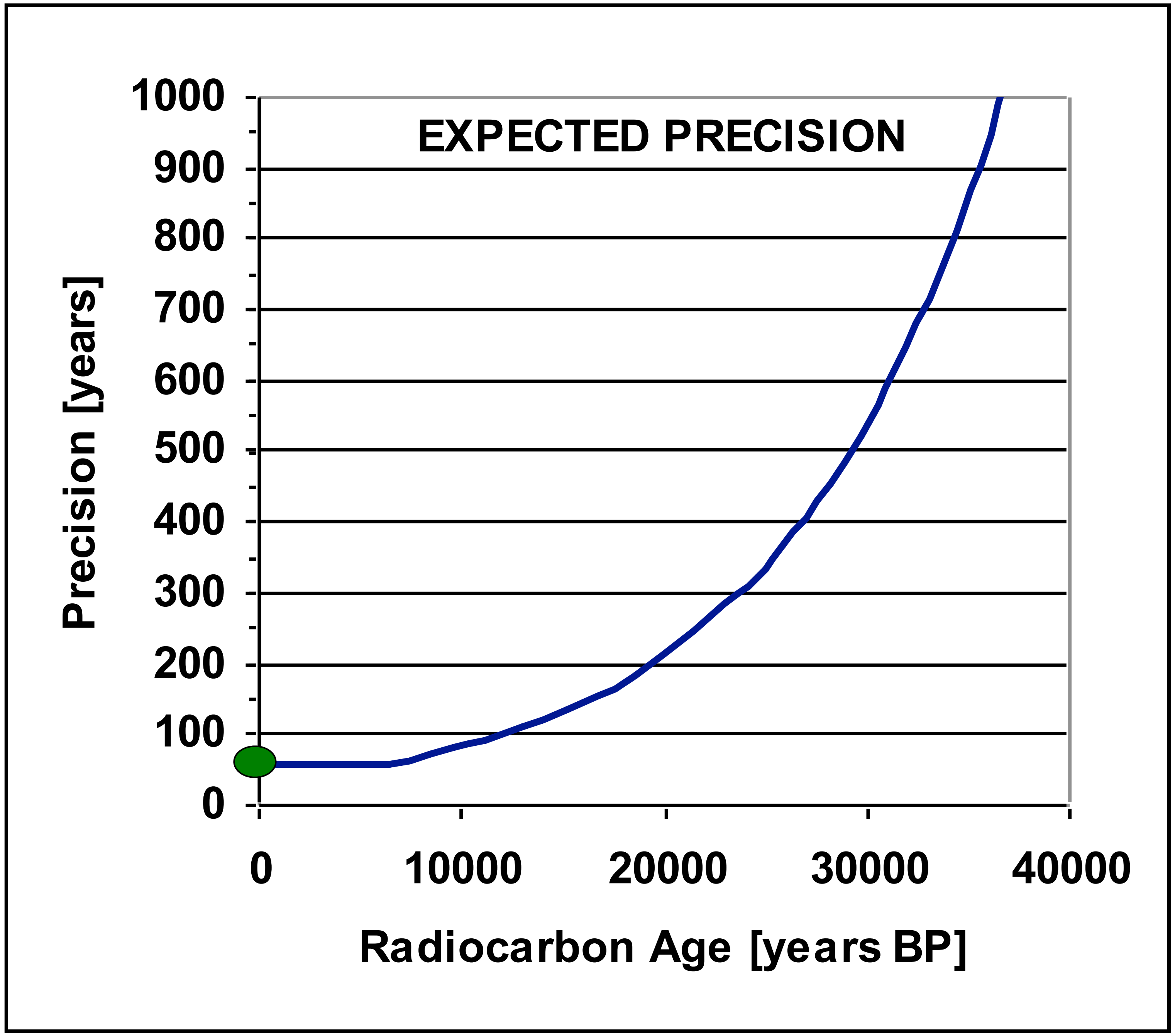


IntCal04 Calibration curve - Last 500 yrs



Age errors and microgram C mass effects

Precision vs radiocarbon age



1 mg, modern ^{14}C level

$$\Delta(^{14}\text{Cage}) = \frac{8033 \cdot \Delta F}{F}$$

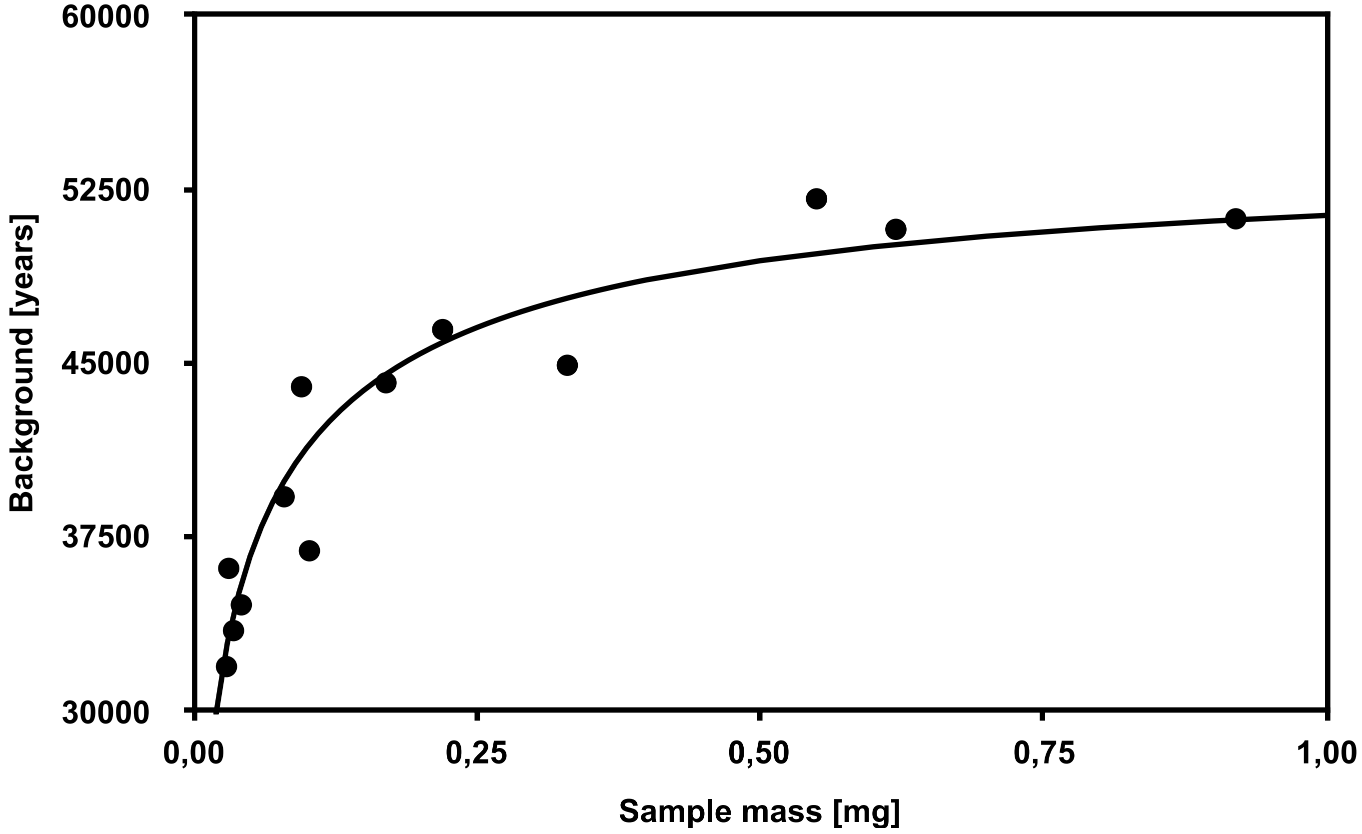
for $\Delta F/F$ = 0.5% →
$\Delta(^{14}\text{Cage})$ = 40 years

Need ~50,000 ^{14}C atoms

For older samples precision decreases

40 ± 1 ka ^{14}C age

Radiocarbon age limit vs sample size

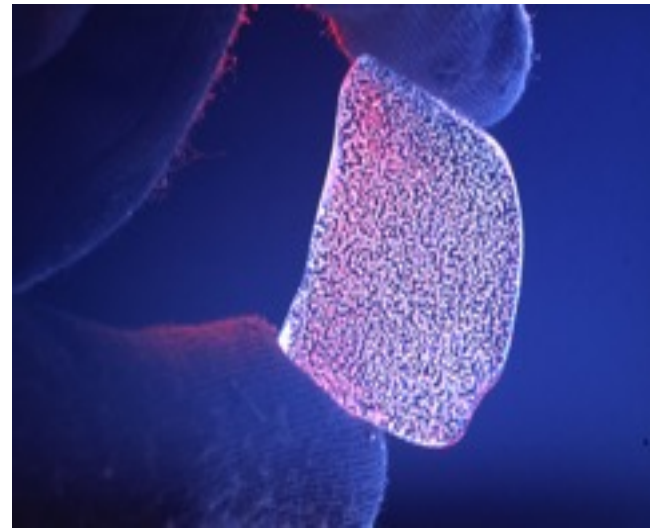


‘dead’ ^{14}C

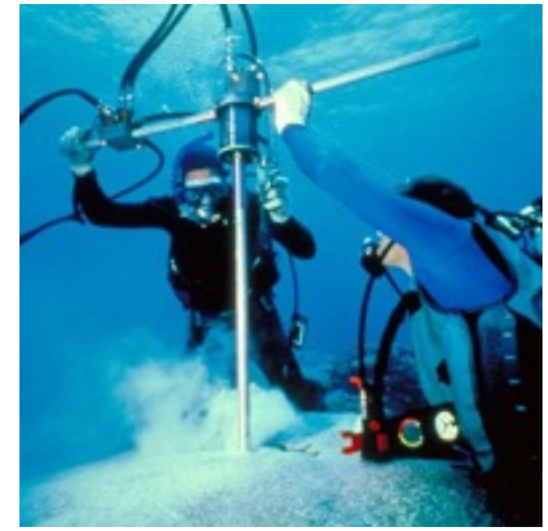
Chemical processing contamination from modern ^{14}C sources

tree-rings,

speleothems

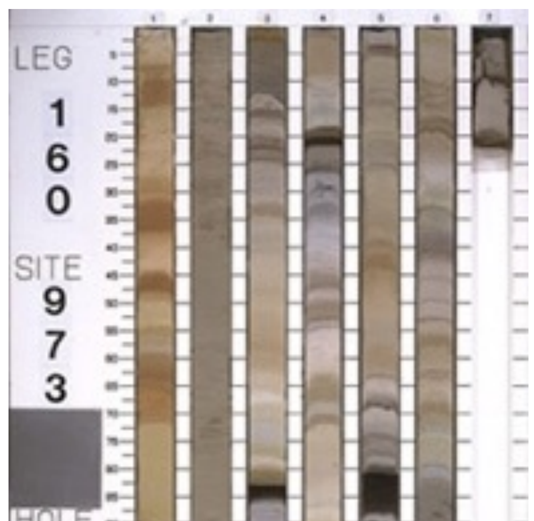


ancient air

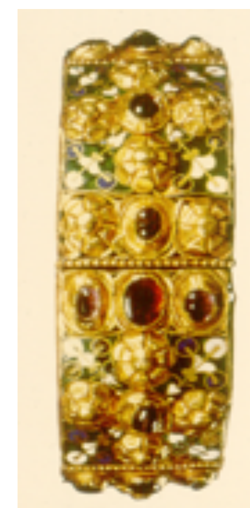


corals

glacial deposits,



ocean/lake sediments



Bomb-pulse dating

Applications of ^{14}C :

dating & tracing

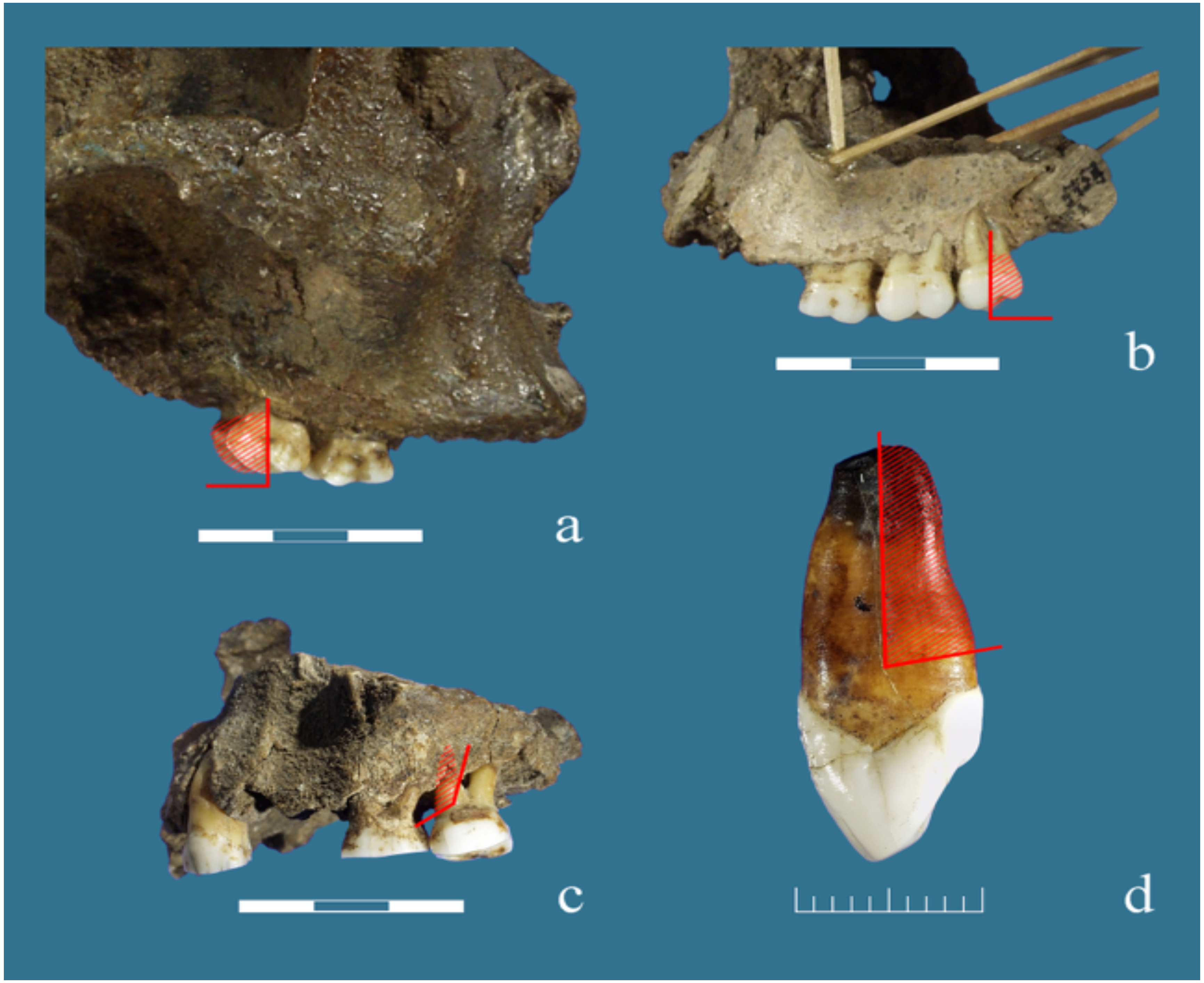
archeology

Radiocarbon dating

Direct dating of Early Upper Paleolithic human remains from the Mladeč Caves in Moravia (Czech Republic)

Eva Maria Wild et al., *Nature* 435 (19 May 2005) 322

Radiocarbon dating

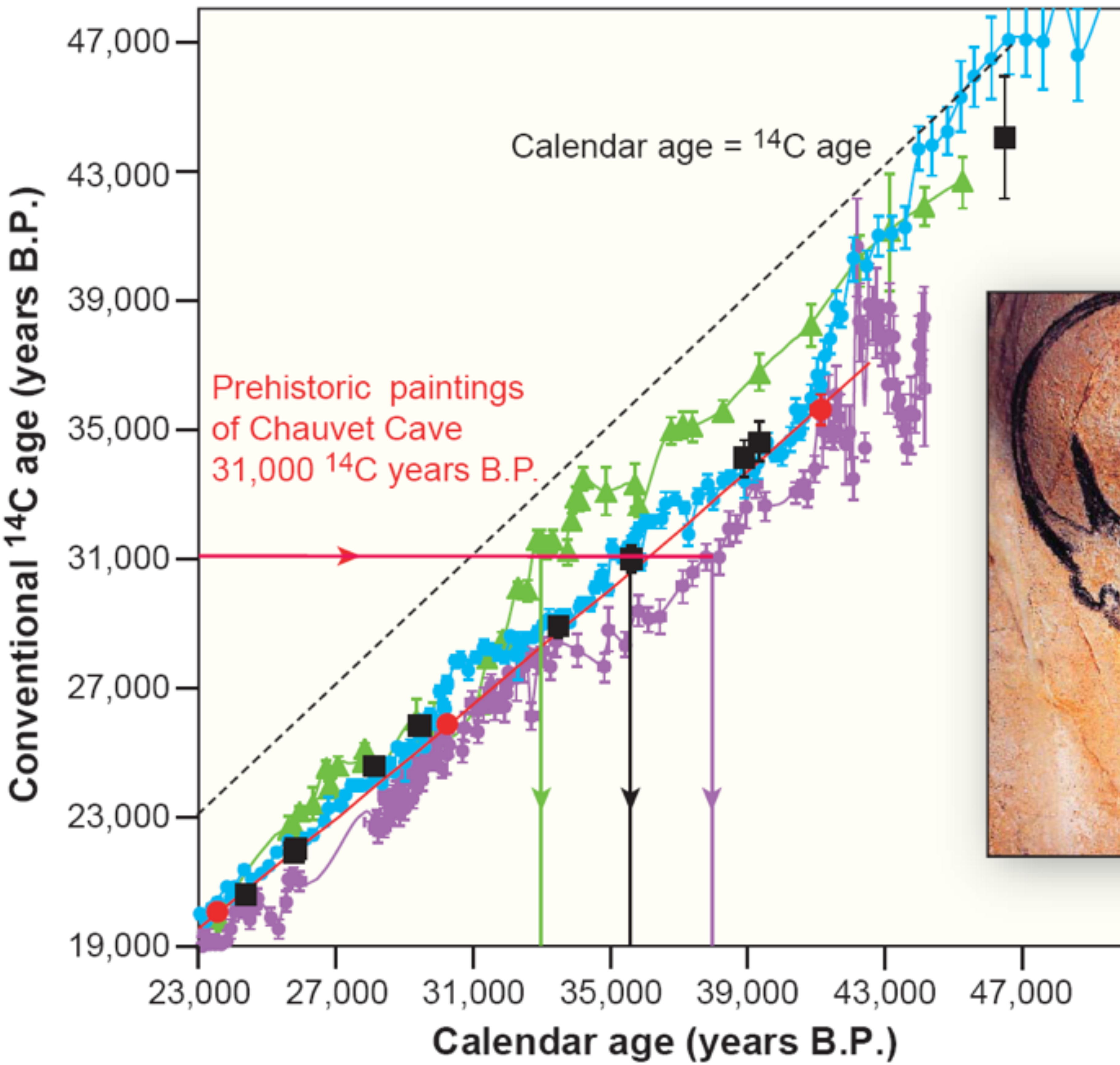


Sampled areas for ^{14}C measurements at VERA

Red Deer Cave, China
A new human species?

D. Curnoe, Plos, 2012

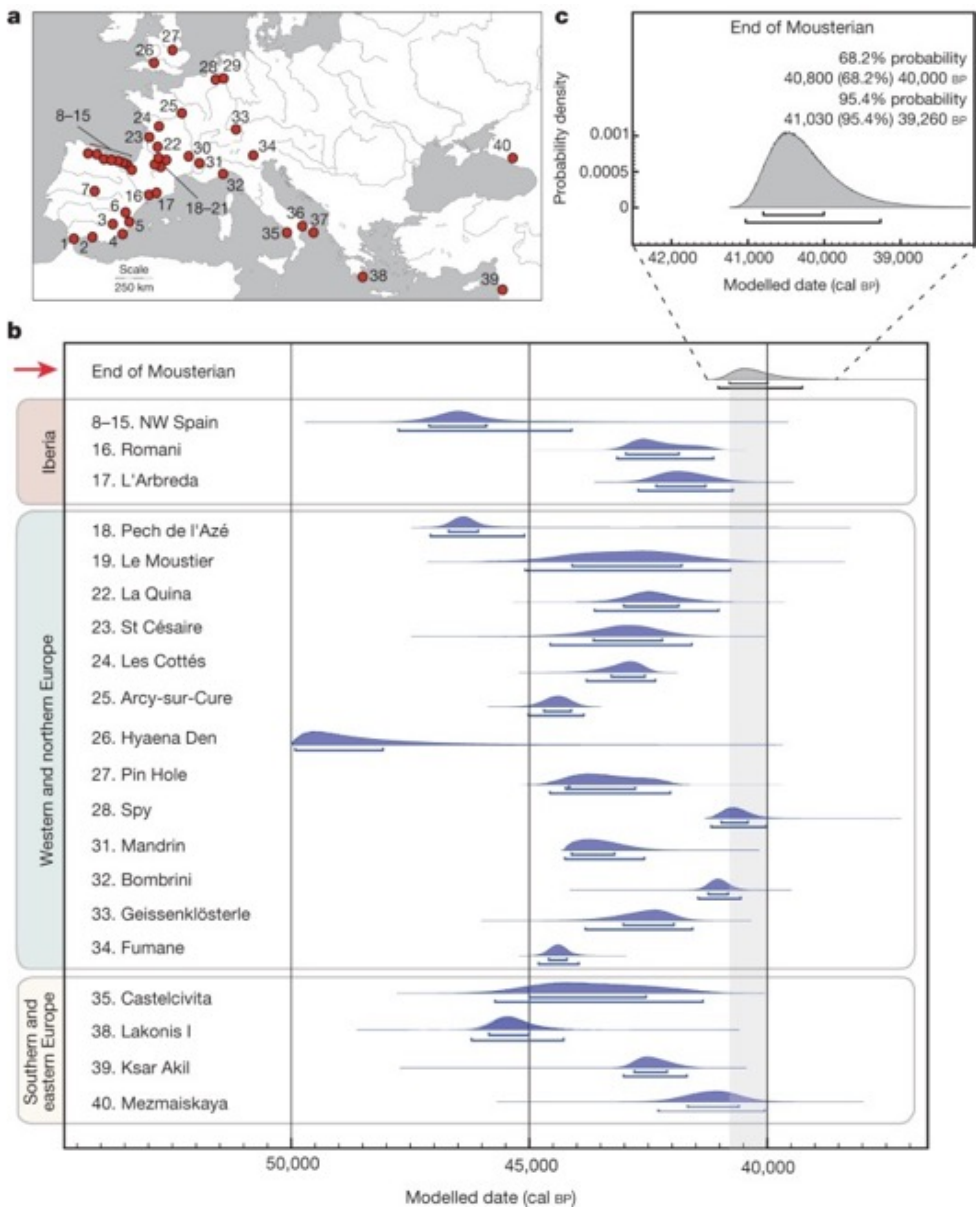
Radiocarbon charcoal from endocranial cavity
11,580 ± 255 cal. yr BP (ANSTO)



Radiocarbon calibration from 23,000 to 47,000 years BP (before present)

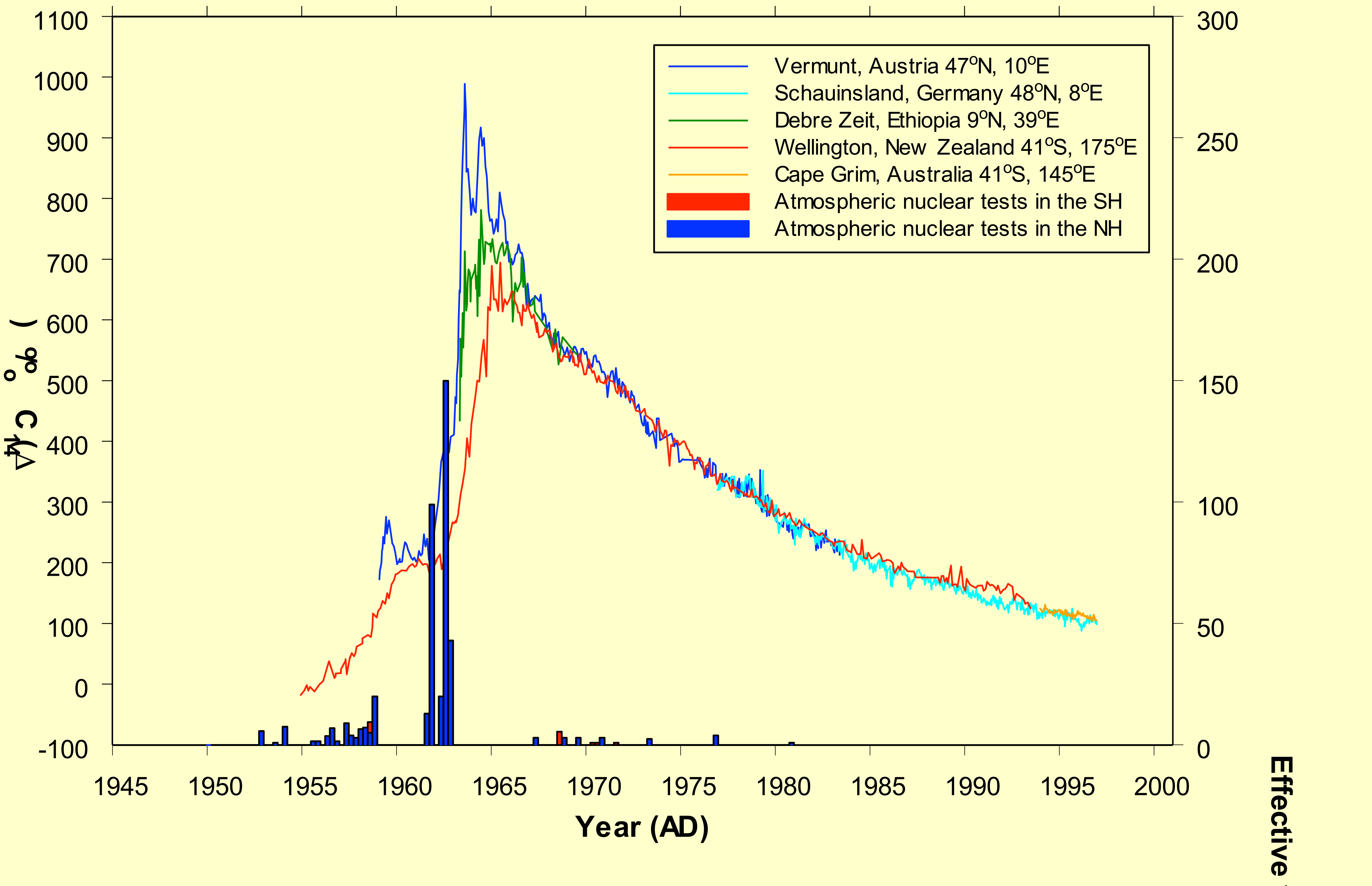
E. Bard et al., *A Better Radiocarbon Clock*, Science **303** (2004) 178

Site locations and final boundary age ranges for Mousterian and Neanderthal sites.

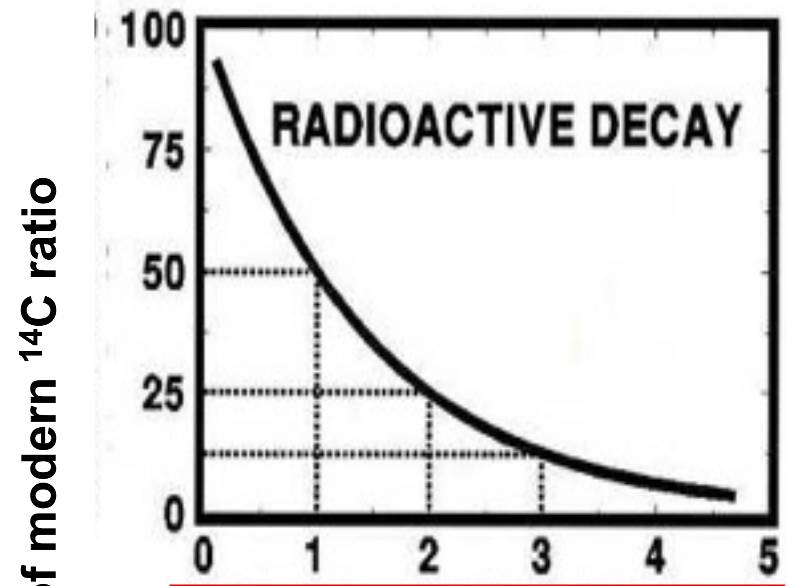


T Higham *et al.* *Nature* **512**, 306-309 (2014) doi:10.1038/nature13621

Atmospheric ^{14}C for the bomb-pulse period



(1) Atmospheric production



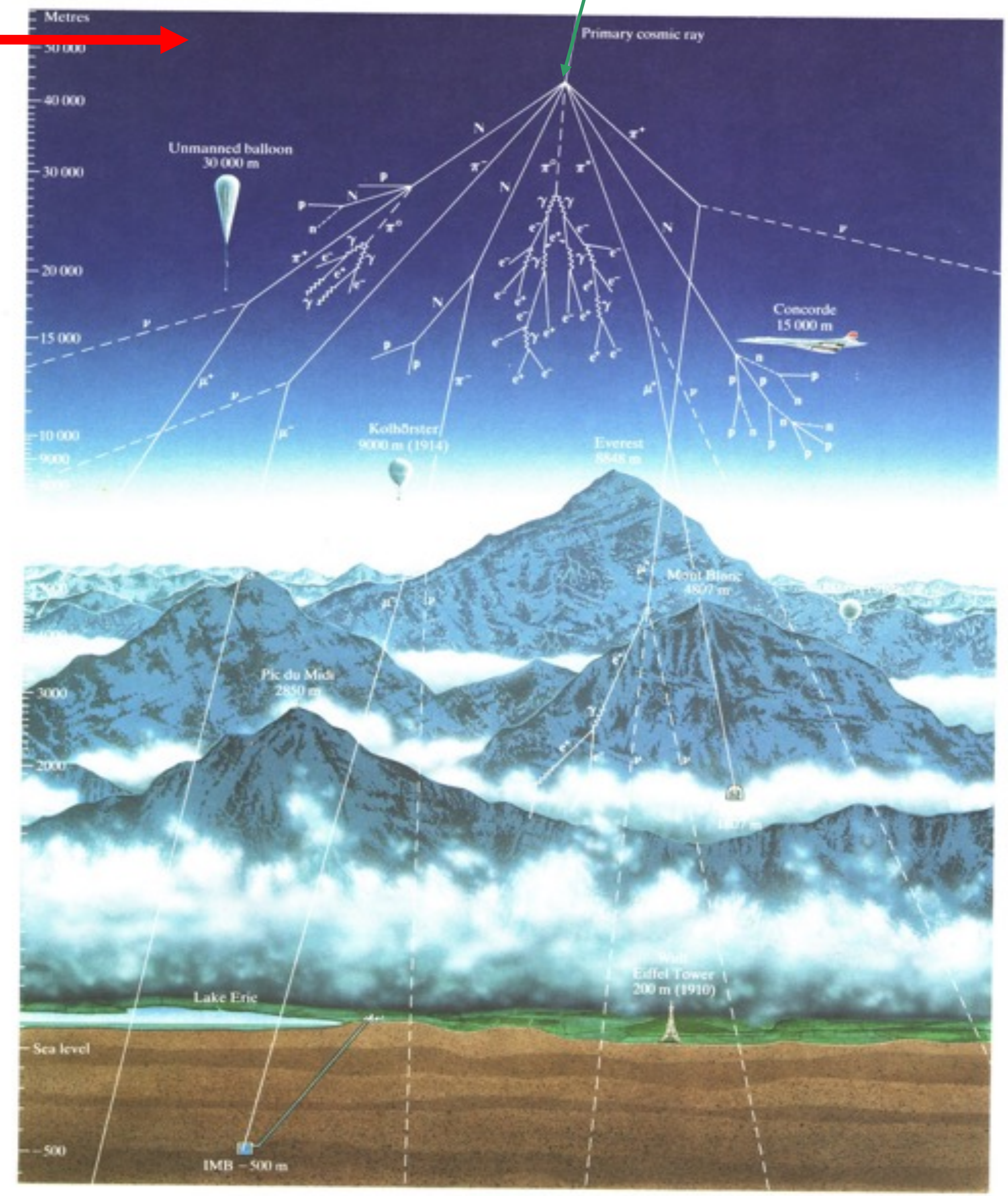
$$C = C_o e^{-\lambda T}$$

T = Radiocarbon dating

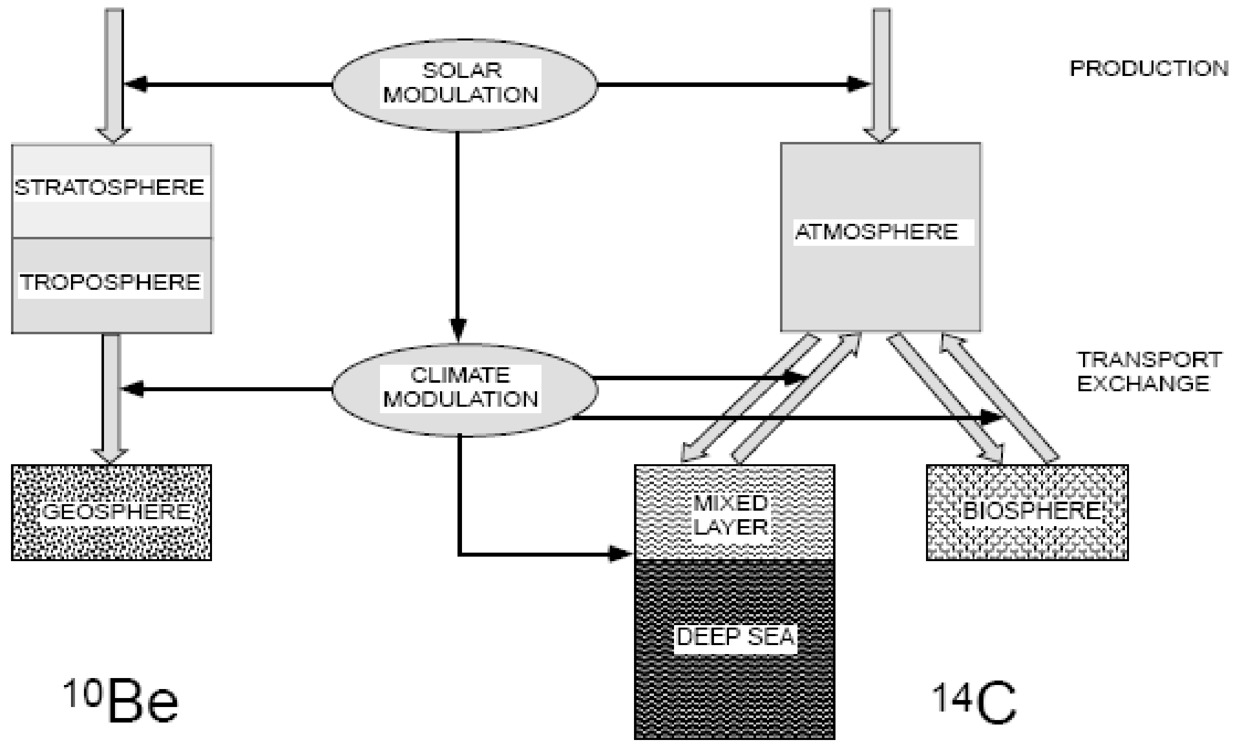
^{10}Be

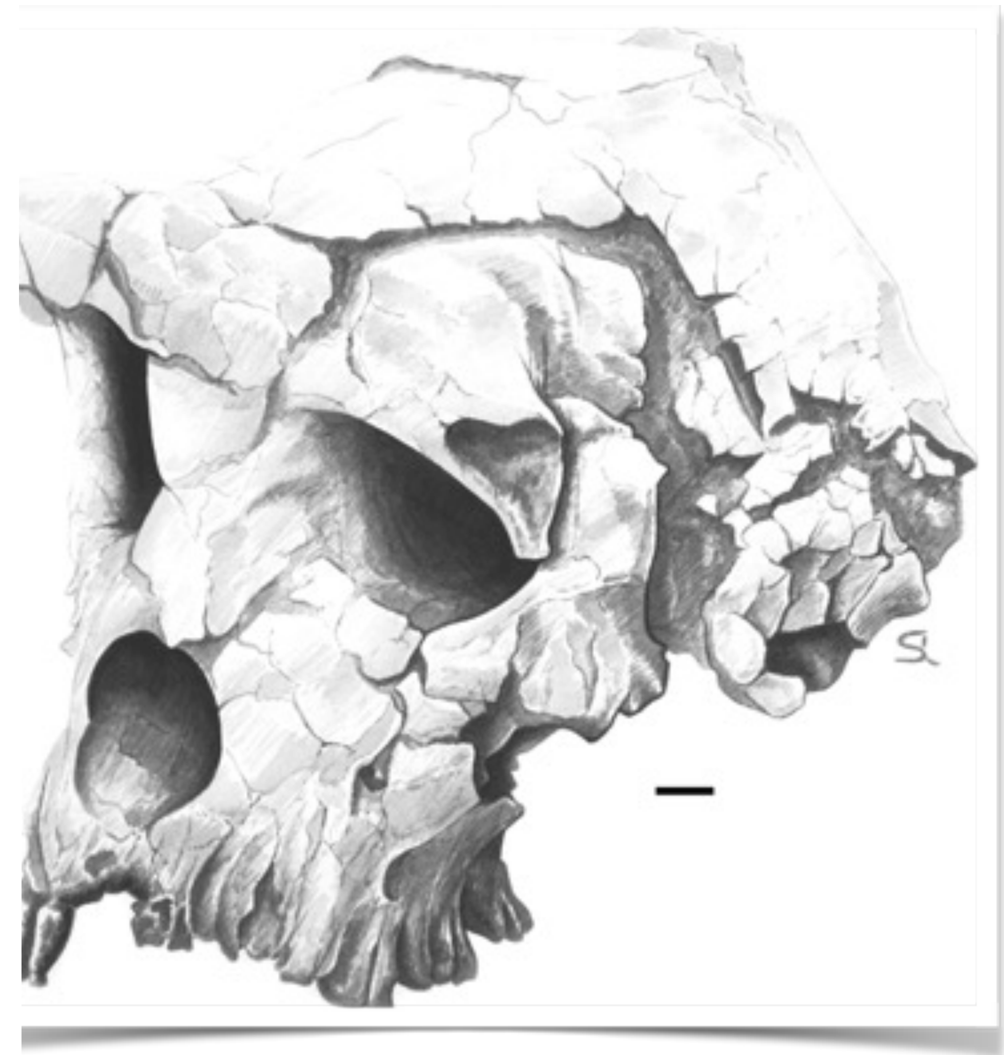
Produced by spallation reactions of primary cosmic rays on N and O

high-energy primary galactic proton



Beryllium-10 Dating





$^{10}Be/^{9}Be$ age
Sahelanthropus tchadensis
6.8 - 7.2 Ma

Cosmogenic nuclide dating of *Sahelanthropus tchadensis* and *Australopithecus bahrelghazali*: Mio-Pliocene hominids from Chad

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PNAS | **March 4, 2008** | vol. 105 | no. 9